A Thesis

entitled

THE CHEMISTRY AND CRYSTAL STRUCTURES OF SOME PHOSPHINO-ETHER COMPLEXES OF RHODIUM AND IRIDIUM

submitted by

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ABBREVIATIONS

Spectral:

i.r.	Infra red
$\nu(cm^{-1})$	Frequency of absorption maximum
s,m,w,sh.	Strong, medium weak, shoulder.
u.v.	Ultraviolet
λ_m(n.m.)	Wavelength of the absorption maximum in n.m.
ϵ	Molar extinction coefficient
n.m.r.	Nuclear magnetic resonance
p.p.m.	Parts per million
t.m.s.	Tetramethylsilane
δ	The delta scale, based on t.m.s.=0 p.p.m.
J(c/s)	Spin-spin coupling constant
s, d, m, q.	Singlet, doublet, multiplet, quartet.

Ligands:

en	Ethylenediamine
dien	Diethylenetriamine
dPm	Bis-diphenylphosphino methane
dPe	Bis-diphenylphosphino ethane
L_1	Bis-1,5(diphenylphosphino)-3-oxa pentane
L_2	Bis-1,8(diphenylphosphino)-3,6-dioxa octane
L_3	Bis-1,11(diphenylphosphino)-3,6,9-trioxa undecane
ppp	Bis-1,3(diphenylphosphino)-2-oxa propane

Note:

Compounds prepared during the course of this work are numbered in arabic script as they appear in text.

CHAPTER 1

CHAPTER 1

INTRODUCTORY CHAPTER

As noted in the abstract, the work in this thesis is concerned with a number of related but relatively distinct areas of chemistry :

(a) The preparation of a variety of linear phosphino-ether ligands. In particular the series of bis phosphines, $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (L_n where n = 1, 2 or 3) were used to investigate both the effect of increasing ligand chain length and the introduction of neutral O donors on the type of complex formed with the group VIII b metals Rh and Ir.

(b) The attempted synthesis of macrocyclic phosphino-ether ligands.

(c) The preparation of Rh and Ir carbonyl and ethylene complexes of L_n in which the ligands function as trans bidentate donors and the preparation of cationic derivatives in which ligand O donors are important in determining the structure of the complex.

(d) The single crystal X-ray structure determinations of the complexes $[RhL_nCO(S)]^+ PF_6^-$ (where S = solvent or is absent).

Accordingly, the introduction has been divided into three sections discussing respectively :

1.1 The importance of phosphorus ligands in organometallic chemistry.

1.2 Macrocyclic crown ethers as binding agents and the change in properties caused by the introduction of heteroatoms.

1.3 Some general aspects of the chemistry of Rh and Ir organometallic complexes and the catalytic properties of group VIII organometallic complexes.

The elementary theory necessary to explain the crystallographic determinations is included in the experimental section of Chapter 4.

SECTION 1.1

The Importance of Phosphorus Ligands in Organometallic Chemistry

1.1.1 Bonding

A variety of phosphorus ligands of the general type PX_3 (where X = alkyl, alkoxy or halogen) as well as the analogous, although less commonly used ligands of arsenic, antimony and bismuth, form complexes with transition metals.[1,2] These donor molecules are good Lewis bases and give adducts with acceptors such as BR_3, in which d orbitals are not involved. However, much of the interest in these ligands arises from their propensity for the heavy group VIII metals and in such compounds the possibility of interaction between empty ligand d orbitals and filled metal d orbitals exists. Chatt[3] was amongst the first workers to classify the general pattern of behaviour of a large number of transition metal ions which show a greater affinity for heavy than for light donor atoms. He defined[3] two broad divisions, Class A and Class B (figure 1.1.1). The Class B metal ions show the following sequence of relative affinities in complex formation :

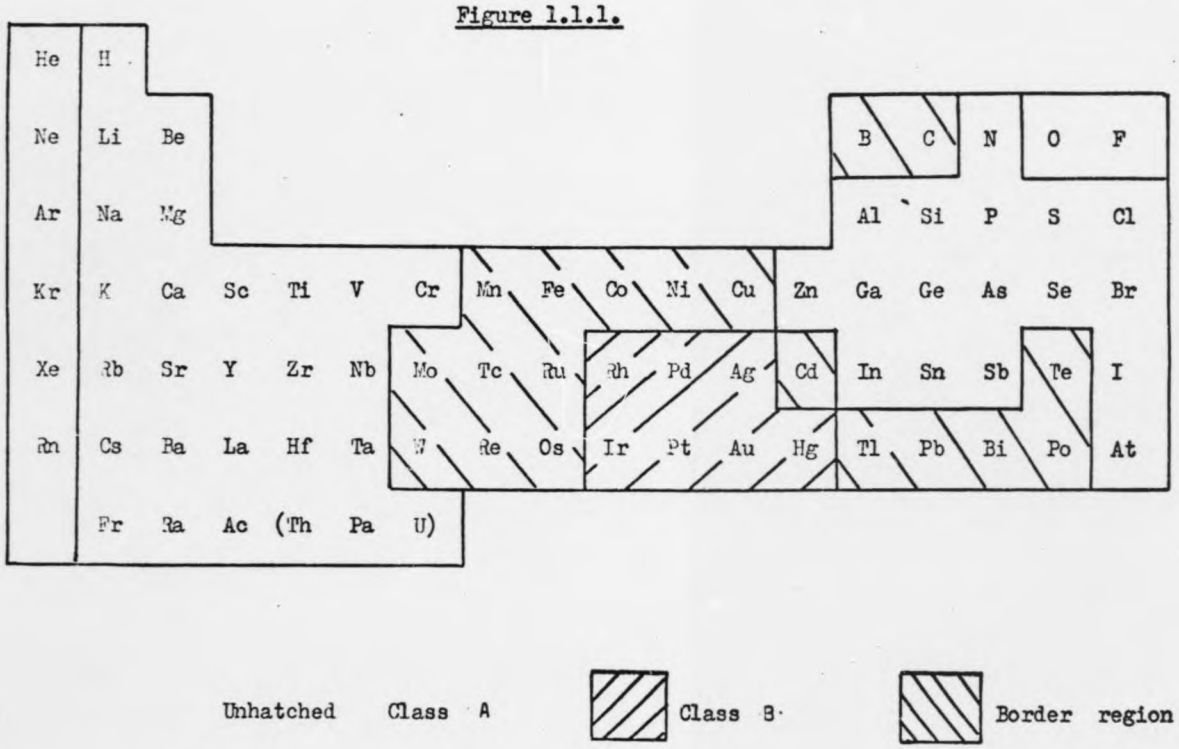
$$N \ll P > As > Sb$$
$$O \ll S \sim Se \sim Te$$
$$F \ll Cl < Br < I$$

A related and extended classification was later proposed by Pearson,[4] who introduced the concept of hard and soft acids and bases. For example, Pearson's 'soft' acids include Chatt's Class B ions (group VIII metal ions) and the soft bases include the heavier donor atoms (P→Bi, S→Te and Cl→I). Such terms are without clear physical meaning, but the gross classification into Class A or B (hard/soft) appears to be controlled by the relative importance of ionic and covalent bonding.[5] A number of attempts have been made to place this theory (colloquially termed "HSAB") on a quantitative basis so that the degree of softness can be expressed numerically.[4,5] In particular, Drago[6] has had considerable success in correlating the enthalpy of complexation, ΔH, with empirical parameters E and C for data obtained in poorly solvating solvents (or better gas phase data) to minimise solvation effects :

$$-\Delta H = E_A E_B + C_A C_B$$

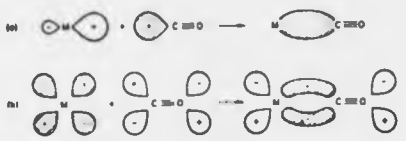
where the subscripts A and B indicate the acceptor and donor respectively, and E and C essentially represent the electrostatic and covalent contributions to bonding.

Figure 1.1.1.

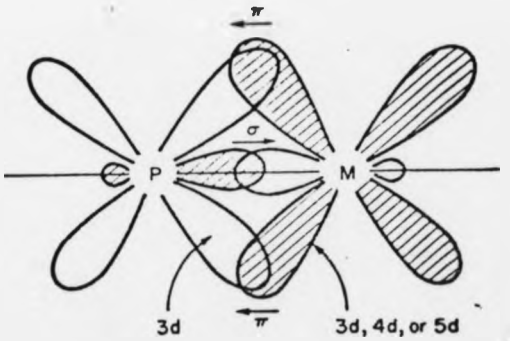


The distribution of Class A and Class B character of metal ions across the Periodic Table. (as Fig. 1 of : S. Ahrland, J. Chatt, and N.R. Davies, Quart. Rev., 1958, 12, 265.)

Figure 1.1.2. Bonding in Metal Carbonyls and Phosphines.



a) The formation of the M←C σ bond using an unshared pair of electrons on the carbon atom. b) The formation of the M→C π bond using metal d orbitals and C≡O antibonding orbitals. Other orbitals are omitted for clarity.



a) The formation of a M←P σ bond using the lone pair on phosphorus. b) The M→P π bond, involving back-bonding from a filled metal d orbital to an empty phosphorus 3d orbital.

As Drago notes,[5] a four parameter equation such as this cannot adequately describe situations in which additional factors such as solvation, π-backbonding or steric effects are important. A study of systems which do not obey the equation may be useful in indicating such effects and will emphasise the amount of experimental data required to introduce a new parameter.

It was initially believed[1] that the preference of Class B or 'soft' metals for phosphorus donors was due to the formation of π-type bonds between the metal and phosphorus atoms. Phosphorus has 3d orbitals of fairly low energy. When the atom to which phosphorus donates has electrons in orbitals of the same symmetry as the empty d orbitals, back donation resulting in overall multiple bond character may result. A schematic representation of this type of bond (dative π-bonding or backbonding) is shown in figure 1.1.2. The extent to which backbonding occurs will depend upon the identity of the donor atom and on the electronegativity of the groups attached to it. Drago cites one case[6] in which π-backbonding may be necessary to interpret ΔH, since the heat of complexation of a cobaloxime-trimethylphosphite adduct is higher (4.8Kcal/mole) than predicted by the E and C equation.

The respective contributions of σ- and π-bonding to the metal-phosphorus bond and indeed to the metal-ligand bonding in general, are of current interest. The problem may be tackled experimentally, particularly by photoelectron spectroscopy and there have been quantum mechanical calculations.

In the case[7] of <u>trans</u> $PtCl_2(NH_3)(PH_3)$, Zumdahl and Drago carried out extended Huckel calculations employing Slater exponents intended to overemphasise $d\pi - d\pi$ interactions. These suggested the Pt-P π-bond strength to be <u>circa</u> 15% of the corresponding σ-bond strength. A more recent <u>ab initio</u> all electron SCF-MO calculation[8] compared $Cr(CO)_5NH_3$ and $Cr(CO)_5PH_3$, but does not permit definitive conclusions about the relative importance of σ- and π-overlap in the Cr-P bond.

The He(I) photoelectron spectra of group VIIIc trifluorophosphine complexes[9] may be analysed to reveal the energies of valence orbitals* as shown :

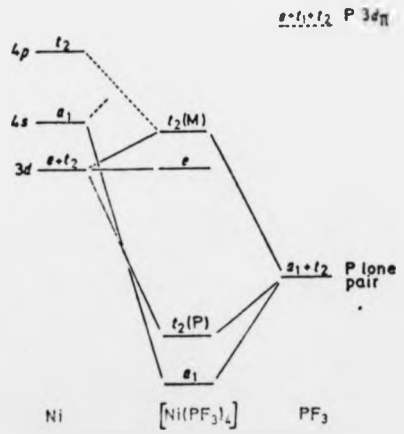
* Vertical ionisation potentials with standard deviations in parentheses.

TABLE 1.1.1

	$Ni(PF_3)_4$	$Pd(PF_3)_4$	$Pt(PF_3)_4$
t_2 (M)	9.69(4)	9.9(1)	9.83(2)
e	10.74(4)	12.2(1)	12.45(1)
t_2 (P)	13.17(4)	13.7(1)	14.54(2)
a_1	14.65(2)		
F lone pair	15.97(1), 17.48(2)	15.84(5), 17.4	15.87(1), 17.53(1)
P - F bond	19.42(1)		19.40(2)

For the nickel complex this data was interpreted in terms of the bonding scheme shown in figure 1.1.3.

FIGURE 1.1.3



The σ-bonding scheme for $[Ni(PF_3)_4]$.

The P - F and F lone pair orbital energies are similar in these complexes to free PF_3 in marked contrast to species such as $F_3P:BH_3$[9] where the shift of ligand ionisation potentials to higher energy implies a polar donor bond.

Indeed it is suggested that the contributions of π and σ components to the M - P bond are (roughly) equivalent. The variations in energy of the valence orbital i.p's implies that both σ- and π-bonding are strongest for Pt and probably weakest for Pd. Furthermore, the variations in the i.p's of the P - M bonding orbitals contrasts with that observed[10] for C - M bonding orbitals in the hexacarbonyls of Cr, Mo and W. Here (in spectra somewhat confused by overlap) it was tentatively suggested that the i.p's of the corresponding t_{1u}, e_g and a_{1g} orbitals were almost invariant to the metal.

Nixon[11] has recorded the photoelectron spectra of $Cr(PF_3)_6$, $Fe(PF_3)_5$ and $HRh(PF_3)_4$, and drawn qualitatively similar conclusions. An attempt[8] to define the relative π-acceptor abilities of $Cr(CO)_5NH_3$ and $Cr(CO)_5PH_3$ by He (I) photoelectron spectroscopy, in conjunction with previously discussed quantum calculations, was complicated by difficulties in accurately relating the extent of ligand contributions to the relevant orbitals.

Studies of core orbital binding energies are complementary to the above work. For example, the X-ray photoelectron spectra[12] of $Cr(CO)_6$ when compared to that of $Cr(CO)_5(PH_3)$ and $Cr(CO)_5(PMe_3)$ shows that the latter have lower C_{1s} and O_{1s} core binding energies consistent with increased occupancy of $\pi^*_{C=O}$ in the latter complexes, possibly indicating stronger σ-donor and/or weaker π-acceptor abilities for the phosphines relative to carbon monoxide. A number of other X-ray photoelectron studies on metal-phosphine complexes support the suggestion that alkyl, aryl or alkoxy phosphines may be better σ-donors and poorer π-acceptors than carbon monoxide. For example, a very recent paper by Grim and Matienzo[13] reported the Mo ($3d_{5/2}$), P (2p) and N (1s) energy levels of a wide variety of phosphine or amine, molybdenum carbonyl complexes. In the series $LMo(CO)_5$, $L_2Mo(CO)_4$ and $L_3Mo(CO)_3$, (where L may be either an alkyl amine or an alkyl, aryl or alkoxy substituted phosphine) the average Mo ($3d_{5/2}$) binding energy decreases as CO is replaced by a phosphine or amine. This indicates a higher electron density on Mo with increasing replacement of CO by better σ-donors and poorer π-acceptors than CO. Furthermore, within a given series, $L_2Mo(CO)_4$ or $L_3Mo(CO)_3$ compounds with nitrogen ligands have lower Mo ($3d_{5/2}$) binding energies than those with phosphines. This is consistent with phosphorus being a better π-acceptor and/or weaker σ-donor than nitrogen. Finally, as has previously been noted,[14] there is little change of the phosphine P (2p) binding energies upon coordination. (In this study a slight (and perhaps

insignificant) increase of circa 0.1 - 0.5 eV was observed on coordination). In contrast, the gas phase X-ray photoelectron spectra of $Cr(CO)_6$ and $LMn(CO)_5$[15] (where L = CH_3, CF_3, H, Cl, Br or I) shows that the C_{1s} and O_{1s} core binding energies are circa 2.5 eV less than the values observed for free CO. This is consistent with π-backbonding being greater than σ-bonding in complexes of this type. It is to be noted that the frequent statements[16,17] to the effect that π-acceptor properties of PF_3 are comparable to or exceed those of CO are inconsistent with these photoelectron studies.

Infrared spectroscopic studies have been widely employed (particularly in the older literature) to delineate the nature of metal-ligand bonds. In a transition metal complex having both CO and potentially π-accepting ligands, there will be competition for the available π-electron density at the metal. This might be expected to cause a change in the degree of π-backbonding to CO with a corresponding change in ν(CO) (and the CO force constant).[18-22] This method has been applied to the series of molybdenum carbonyls, cis-$Mo(CO)_4(R_{3-n}PX_n)_2$ (where R = alkyl, aryl, alkoxy and X = H, F, Cl and n = 0, 1, 2, 3),[23] and shows that increasing the electronegativity of the substituents attached to phosphorus causes a progressive shift of the CO stretching frequencies towards the value of uncomplexed CO (ν(CO) = 2143 cm^{-1}). Nitrogen which does not have d orbitals of suitable energy for π-bonding has significantly lower values for ν(CO) :

TABLE 1.1.2

CO stretching frequencies** (cm^{-1}) for the complexes cis-$Mo(CO)_4(L)_2$, from reference 23

Ligand L	A_1^1	A_1^2	B_2 and B_1*
NH_3	2010	1837	1915, 1780
Me_3P	2016	1910	1896, 1874
Ph_3P	2023	1929	1911, 1899
$(MeO)_3P$	2037	1945	1926, 1921
PH_3	2040	1947	1925, 1897
$MePCl_2$	2056	1991	1959, 1959
PF_3	2091	2022	2022, 2003

* The assignment of these bands is uncertain.

** Measured in solution in various solvents, see reference 23 for further details.

In this same paper,[23] the authors correlate the CO force constants of a series of phosphine carbonyl complexes with the first vertical ionisation potentials of the respective phosphines, obtained from the He (I) photoelectron spectra. They derive a scale of π-acidity from this correlation which is in qualitatively good agreement with that of an earlier (and broader based) study,[18] which indicated the following order of π-acidity :

$$CO \sim PF_3 > PCl_3 \sim AsCl_3 \sim SbCl_3 > PCl_2(OR) > PCl_2R$$
$$> PCl(OR)_2 > PClR_2 > P(OR)_3 > PR_3 \sim AsR_3 \sim SbR_3$$
$$> RCN > NR_3 \sim OR_2 \sim ROH > H_2NCOR$$

A very extensive ranking of PX_3, PXX'_2 and $PXX'X''$ ligands based upon the A_1 CO stretching frequency of $PX_3Ni(CO)_3$ has been carried out.[24,25] In another study,[26] the CO force constants k_1 (radial) and k_2 (axial), for a series of octahedral carbonyls, cis-$M(CO)_4L_2$ (where L_2 is a bidentate N, P, As or S donor and M = Cr, Mo, or W), were obtained by an iterative procedure from the four CO stretching frequencies. The interpretation of this force constant data indicated the following, generally accepted, order of π-acidity :

$$P \sim As > S > N$$

Whilst i.r. correlations such as these strongly imply that phosphorus has significant π-acidity, they do not prove it. Other experiments[27] indicate that the soft character of phosphorus need not be due to π-bonding effects alone and that σ-bonding effects involving changes in the s component of the M - P bond may be equally important.

Venanzi[27] and coworkers have reported the $^{195}Pt - ^{31}P$ coupling constants for a series of square planar Pt(II) and Pt(IV) complexes. They find that as the ligand trans to phosphorus becomes a better trans director, the $^{195}Pt - ^{31}P$ coupling constant decreases, which they interpret as resulting from a reduction of the s character and strength of the Pt - P bond. Furthermore, the ratio of the $^{195}Pt - ^{31}P$ coupling constant in the cis complex to that in the trans complex is the same for both Pt(II) and Pt(IV) complexes. It was suggested that since π-bonding is expected to be much less in Pt(IV) than in Pt(II) complexes, the similar coupling constant ratios for the two types of complex indicate that π-bonding is unimportant in both. It must be borne in mind that interpretation of coupling constant data is

far from simple. Venanzi et al. used an approximate expression for J(Pt - P), based only upon the Fermi contact term. Substantial corroborative data is necessary to prove the validity of this interpretation.

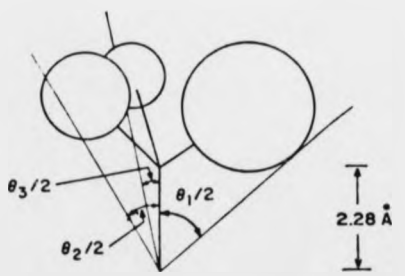
In conclusion, it is clear that π-bonding is very important in phosphorus ligands with strongly electronegative substituents such as PF_3, particularly when used in conjunction with Lewis acids of low formal oxidation state, as in the complex $Pt(PF_3)_4$. The importance of π-backbonding decreases with increasing alkyl substitution, as indicated by indirect spectroscopic studies. Whilst the ligands PF_3 and CO are known to form a variety of analogous metal complexes, the available evidence indicates that bonding in these ligands is not directly comparable and should not be treated as such.

The studies described relate to the electronic and spectroscopic properties of metal-phosphorus bonds. In considering bond energies and complexation equilibria, steric effects are important to a degree, dependent on the metal and coordination geometry.

In one extreme case Tolman demonstrated that steric factors can dominate the position of equilibria in $Ni(PR_3)_n(CO)_{4-n}$ complexes.[25a] More often both steric and electronic factors are important and it has been noted[25c] that such effects have been correlated with a wide variety of phenomena including stabilities, fluxional behaviour, rate constants and catalytic activity and specificity in product formation.[25c]

Tolman defined a steric parameter called the cone angle.[25a,b] For any $PR_iR_2R_3$ ligand this may be defined by reference to the following equation and figure 1.1.4 :

FIGURE 1.1.4



cone angle, $\theta = \frac{2}{3} \sum_{i=1}^{3} \frac{\theta_i}{2}$

where $\frac{\theta_i}{2}$ is the half angle of the ith substituent defined by the metal-phosphorus axis and an outermost van der Waal's contact. Tolman has suggested[25b] that this method may be extended to bidentate P-donors by letting $\frac{\theta_i}{2}$ be the angle between one P-M bond and the bisector of the PMP angle; little work has yet been reported on the use of this method. Tolman estimates cone angles by minimising steric interactions in molecular models and measuring the resultant cone angle with a simple jig.[25a] Large errors, as great as $\pm 10^{\circ}$ in certain cases, are involved. Recently an empirical n.m.r. method of estimating cone angles has been reported.[25c] The chemical shift of the methyl resonance of coordinated methanol in trans-$\left[L\,Co(DH)_2(CH_3OH)\right]^+$, where $L = RR'_2P$ (R = or ≠ R' = alkyl, aryl, alkoxy or phenoxy) and DH = monoanion of dimethylglyoxime, is shown to be related to the Tolman cone angle by the empirical expression:

$$\text{cone angle} = \sum_{i=1}^{4} C_i \left[1.0 - \frac{0.15}{(\tau - 7.0)} \right]^{i-1}$$

where C_i are constants, τ = chemical shift of the methanol methyl group and the cone angles used are > 118°.

With some exceptions values of cone angles from n.m.r. data agree well with those of Tolman and it has been noted that some anomalies in earlier work disappear when the revised values are used. A further test of n.m.r. cone angles is provided by a recent paper by Tolman.[25d] Here the enthalpies of the following reaction were measured for 34 group V donor ligands:

$$\text{trans-}\left[CH_3PtQ_2(THF)\right]^+ + L \longrightarrow \text{trans-}\left[CH_3PtQ_2L\right]^+ + THF$$

where excess L was used and when the cone angle of L was > 140 some cis products are formed. Q = $P(CH_3)_2(Ph)$.

The enthalpy is clearly dependent upon the size of L and decreases smoothly as shown in the following series (Table 1.1.3). It is also shown that electronic effects cannot be neglected when substituents of high electronegativity are present.

TABLE 1.1.3

L	$-\Delta H$ (Kcal/mol)	Cone Angle* (°)
$P(CH_3)_3$	26.2	118 (< 117)
$P(C_2H_5)_3$	24.3	130 (---)
$P(CH_2C_6H_5)_3$	23.2	165 (130)
$P(i\text{-}C_3H_7)_3$	12.7	160 (164)
$P(t\text{-}C_4H_9)_3$	4.8	182 (---)

* Values in parentheses are estimated by n.m.r. in reference 25c.

In the case of $P(CH_2C_6H_5)_3$ there can be little doubt that the n.m.r. cone angle value is significantly better. Unfortunately in some instances n.m.r. cone angles, particularly that of Ph_3P appear overestimated; thus further work is required on this promising method.

Despite Tolman's convincing demonstrations of the importance of steric effects, they have often been neglected. An example of some importance has recently been reported by Palenik et al.[28] It is shown that the mode of thiocyanate coordination in palladium thiocyanate-phosphine complexes is determined by steric rather than electronic effects. The X-ray crystal structures of the series cis- $[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]Pd(CNS)_2$ (for n = 1, 2 or 3) were determined. The thiocyanate coordination changes from S,S when n = 1 to S,N for n = 2 and N,N with n = 3. A comparison of the angular changes in the 3 complexes together with an examination of a large amount of crystallographic data on Pd complexes indicates:

1. As n increases the thiocyanate coordination sites are subjected to increased steric hindrance which is the main reason for the change from S-bonded (bent) to N-bonded (linear) thiocyanate.

2. Previous examples of N-bonded thiocyanates which have been rationalised on the basis of antisymbiosis[29] or π-backbonding[29] may actually represent steric effects and should be reconsidered at least in the Pd case.

3. For palladium compounds at least, the variations in bond lengths as a function of the trans atom need not necessarily be a π-effect transmitted across the metal atom. For the three complexes studied here the most consistent explanation of the data involves no π-interactions between the phosphine and sulphur ligands and metal. This supports the earlier n.m.r. results reported by Venanzi[27] for Pt(II) complexes.

1.1.2 Types of Phosphorus Ligand in Common Use

Early work on phosphorus transition-metal complexes shows an almost arbitrarily widespread use of the ligand PPh_3. The reasons for this are obvious since this ligand is commercially readily available as an air stable* crystalline compound whilst alkyl, alkoxy or halogeno phosphines are very air sensitive, noxious ligands which are often not readily available and are unpleasant to synthesise. It is fortuitous that the balance of donor/acceptor and steric qualities of PPh_3 are ideal for a variety of important catalytic complexes, such as $RhCl(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$. More recently the varying donor qualities of PX_3 ligands have been used to modify and explore the oxidative reactivity of transition metal complexes such as the series trans-$Ir(Cl)(CO)(PX_3)_2$.[30] Qualitatively it is found that increasing the Lewis basicity of the ligand increases oxidative reactivity.

There has been a rapidly increasing interest in the use of polydentate phosphines and analogues of the well known chelating amines, en, dien and tren have been synthesised. Such chelating ligands are known to have a number of interesting properties :

(a) They reduce the tendency for ligand dissociation.

(b) They allow greater control of the final stereochemistry of metal complexes.

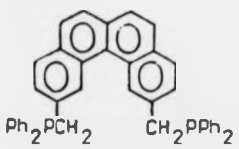
(c) In favourable cases they allow a greater number of ligand donors to coordinate to the metal atom, thereby increasing its Lewis basicity and promoting oxidative reactivity.

Some of the most important types of chelating phosphorus ligands are

* In the absence of light

FIGURE 1.1.5

Types of Phosphorus Ligand in Common Use

Ligand = L		Ref.
Containing one P-donor		
$R_2P(CH_2)_n\text{-}CH=CH_2$ where n = 1, 2 or 3, R = Ph or Et	Ligands of this type are flexible and can act either as monodentate P-donors, e.g. $Mo(CO)_5(L)$ or as bidentate donors, e.g. $Mo(CO)_4(L)$	34
o-$Ph_2P\cdot C_6H_4\cdot CH=CH\cdot CH_3$ o-$Ph_2P\cdot C_6H_4\cdot CH_2CH=CH_2$ o-$Ph_2P\cdot C_6H_4\cdot CH=CH_2$	These are more rigid ligands of some potential interest in catalysis. They are known to form both monodentate P-donor complexes and bidentate chelate complexes, e.g. the trigonal bipyramidal complexes $M(CO)_3(L)$, where $L = Ph_2P\cdot C_6H_4\cdot CH=CH_2$ are known for M = Fe or Ru	35
Containing two P-donors		
$R_2P(CH_2)_nPR_2$ where n = 1 to 10 and R = Ph, Me or cyclohexyl	These give monodentate complexes, e.g. $Ni(Cl)_2(Ph_2PCH_2PPh_2)_2$; cis-bidentate complexes, e.g. $Pd(Ph_2P(CH_2)_nPPh_2)(SCN)_2$ where the mode of thiocyanate attachment changes along the series n = 1, 2 or 3; trans-bidentate complexes, e.g. $M(R_2P(CH_2)_nPR_2)(Cl)(X)$, where n = 9 or 10 and X = Cl for M = Pt and X = CO for M = Ir	36 28 37
$Ph_2P\cdot CH=CH\cdot PPh_2$	A cis-bidentate donor in which steric constraints prevent the alkene from acting as a donor. Both square planar and trigonal bipyramidal complexes are known, e.g. $Ni(L)X_2$, where X = Cl, Br I or NCS and $Ni(L)_2X$ where X = Cl, Br or I	38
o-$PR_2\cdot C_6H_4\cdot PR_2$	A rigid bidentate donor which forms cis complexes, e.g. $(Au(L)_2)^+Cl^-$.	39
	This ligand was synthesised to act as a trans bidentate donor and is known to form complexes such as trans-(MX_2L), where M = Ni, Pd or Pt and X = Cl, Br or I.	40

continued .....

		Ref.
$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$	This ligand can either act as a cis or trans bidentate donor depending upon its length. Known complexes of this ligand are discussed in text, see Chapter 3 section 3.1 and figure 3.1.1.	31
$Ph_2P(CH_2)_2X(CH_2)_2PPh_2$ where X = N or S	These ligands can function as mixed tridentate donors and several five coordinate nickel complexes have been reported, e.g. $Ni(L^*)Br_2$ and $Ni(L^{**})I_2$ where X = N in L^* and X = S in L^{**}.	32 33
$Ph_2PCH_2CH_2PR\,Ph$ $Ph_2P(S)CH_2P(O)Ph_2$	These are assymetric bidentate P-donors and form complexes in which the ligand functions as a bidentate, bridging or monodentate donor, e.g. $LM(CO)_4$, $(CO)_5M\text{-}L\text{-}M(CO)_5$, $LM(CO)_5$, where M = Cr, Mo, W	41 42 43
Containing three P-donors		
$R_2P(CH_2)_nP(CH_2)_nPR_2$ (R) n = 2, 3 $PhP(o\text{-}C_6H_4PPh_2)_2$	Numerous papers have been published by King et al describing the synthesis and metal complexes of tritertiary (and polytertiary phosphines). For example, King shows that $R_2P(CH_2)_nP(CH_2)_nPR_2$ may function as a mono-, bi- or tridentate ligand.	44
Tripod Ligands		
$P(o\text{-}C_6H_4PPh_2)_3$ $N(o\text{-}CH_2CH_2PPh_2)_3$	A wide variety of ligands of this type are known. They are often observed to function as tetradentate donors forming five coordinate trigonal bipyramidal complexes, e.g. $[Ir(Cl)(P(o\text{-}C_6H_4PPh_2)_3)]$	45 46 47

presented in figure 1.1.5. Of particular interest are mixed donor ligands such as $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1, 2, 3),[31] $Ph_2P(CH_2)_2N(CH_2)_2PPh_2$[32] and its sulphur analogue[33] which have the potential for forming mixed donor complexes depending upon the metal requirements. These are discussed in more detail in the introduction to Chapter 3.

The work described in this thesis throws some light on the wide variety of chelate complexes formed by the potentially polydentate series of phosphinoethers $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1, 2 or 3).

SECTION 1.2

Macrocyclic Crown Ethers as Binding Agents and the Change in Properties Caused by the Introduction of Heteroatoms

Introduction

A major development in the field of macrocyclic polyether chemistry was the publication by Pedersen in 1967[48] of the synthesis of over fifty cyclic polyethers, ranging in size from 9 (3 oxygens) to 30 (10 oxygens) atoms. Subsequently the literature on such organic complexing agents has become enormous and volume 16 of 'Structure and Bonding' is devoted to reviewing various aspects of the chemistry of such ligands. Pedersen noted that certain of these compounds exhibited a marked selectivity towards alkali metal ions which was similar to the behaviour of some antibiotics, and this provided impetus for further work in this area. For example, valinomycin is capable of actively transporting K^+ across mitochondrial membranes[49] and an extensive literature exists on the selective complexation and transport of alkali metal ions by naturally occurring macrocyclic compounds[50] (e.g. valinomycin, monactin, enniatin B, etc.). X-ray crystal studies on naturally occurring[51] and synthetic ligand* complexes of this type confirm their basic similarity and it is found that the alkali metal cation is situated at the centre of inwardly orientated oxygen donor atoms.

The large affinity of certain cyclic polyethers for alkali metal ions is somewhat unexpected since ethers are generally considered poor complexing agents unless very strong Lewis acids are present. However, macrocyclic polyethers have been shown to strongly complex many cations besides alkali metal ions, especially in less polar solvents (e.g. Ba^{2+}, Ag^+, Hg^{2+}, Pb^{2+}, etc.).[52] It is well known that group VIII transition metals show a very marked preference for the Class B or soft donors and therefore not surprising that the cyclic polyethers show little or no tendency to complex such metal ions. In order to remedy this it is necessary to introduce softer donor atoms. The synthesis of polythia-[53] and polyaza-ethers[54] achieved this in part and extended the number of heavy metals complexed by macrocyclic compounds (e.g. Cu, Co, Tl, Rh). We have been interested in the attempted production of cyclic polyphosphino

* See section 1.2.2 F and references therein.

ethers since, as discussed in section 1.1, phosphorus is a particularly good donor for group VIII transition metals. Accordingly, in this account, emphasis is placed on the basic properties of crown ethers and how these are modified by the introduction of softer donor atoms. This necessitates the exclusion of much information specifically concerned with alkali metal cations, such as their relevance to ion transport in membranes and potential in organic synthesis. Moreover, many of the design criteria for cyclic polyethers are based upon purely electrostatic bonding considerations and may be inapplicable in the construction of ligands to complex transition metals, which typically have strongly directed bonds with appreciable covalent character.

1.2.1 Some Examples of Macrocyclic Polyether Ligands and Nomenclature

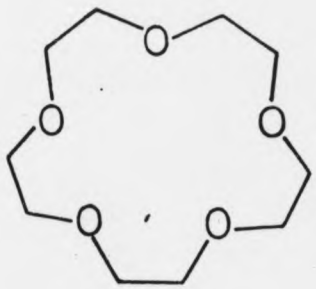
Many macrocyclic compounds containing oxygen, nitrogen and sulphur donor atoms are known. These may be divided into the following categories in which some representative examples are given :

(i)	O donors,	references 106, 94
(ii)	O and N donors,	references 107, 108
(iii)	O and S donors,	reference 109
(iv)	N and S donors,	reference 110
(v)	O, N and S donors,	reference 69
(vi)	N donors,	references 66, 67, 110
(vii)	S donors,	reference 68
(viii)	Reviews,	reference 55

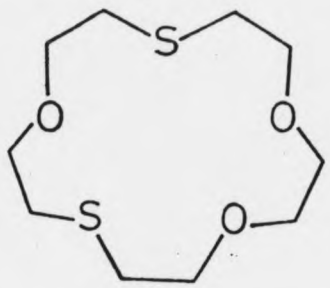
Alkali metal and alkali earth metal cation complexes of such ligands almost invariably involve donor binding sites separated by two carbon atoms. Examples of some of the best known monocyclic ligands are given in figure 1.2.1. Conventional IUPAC rules for naming organic compounds results in the assignment of unequivocal, but complicated names for such compounds.[55] Accordingly, Pedersen's trivial "crown" nomenclature is used, as shown in figure 1.2.1.

Lehn and Sauvage[56] were responsible for introducing a very large class of macrobicyclic amine ligands. These are frequently referred to as 'cryptates' (figure 1.2.2).

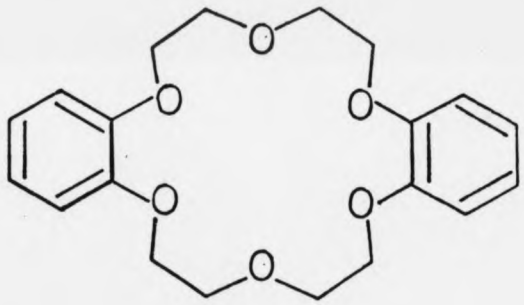
Figure 1.2.1. Representative Crown Ethers and Nomenclature



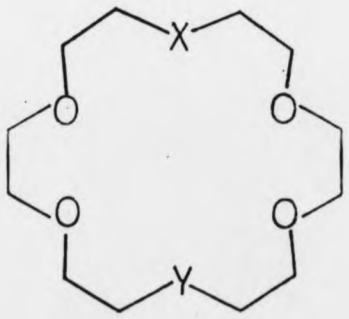
15-Crown-5



1,7-Dithia-15-Crown-5

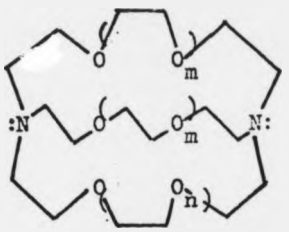


Dibenzo-18-Crown-6

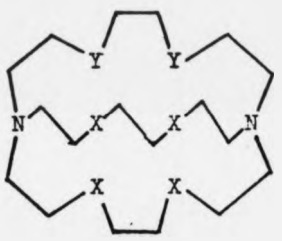


X=Y=O		18-Crown-6
X=NH,	Y=O	Aza-18-Crown-6
X=Y=NH		1,10-Dithia-18-Crown-6
X=Y=S		1,10-Dithia-18-Crown-6

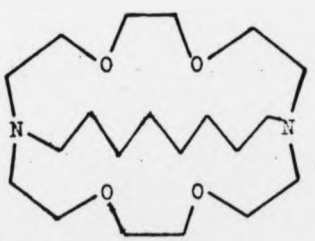
Figure 1.2.2. Representative Bi-cyclic Ligands or Cryptates



(1.1.1.) m:n:0
(2.1.1.) m:0; n:1
(2.2.1.) m:1; n:0
(2.2.2.) m:n:1
(3.2.2.) m:1; n:2
(3.3.2.) m:2; n:1
(3.3.3.) m:n:2



(2o.2o.2s) X:O; Y:S
(2o.2os.2s) 3X:O; X 2Y :S
(2o.2s.2s) X:S; Y:O
(2s.2s.2s) X:Y:S
(2o.2o.2n) X:O; Y:N-CH_3
(2o.2o.2n) X:N-CH_3; Y:O



(2.2.C_8)

Systematic naming of bi-cyclic amines is long and complicated. J.-M. Lehn designates each ligand by a symbol, as shown, which gives the number and nature of the heteroatoms and other structural variations of the bridges.

1.2.2 Variation of Thermodynamic Quantities with Cation and Ligand Parameters

The values of the equilibrium constant K for the reaction :

$$M^{n+} + L \overset{K}{\rightleftharpoons} ML^{n+}$$

are frequently used as a measure of cation selectivity by macrocyclic ligands. The principal experimental methods used to determine log K values have been :

(a) Calorimetry, references 55, 57, 58.

(b) Potentiometric measurements with ion selective electrodes, references 52, 69.

(c) Nuclear magnetic resonance techniques have been used to elucidate the mechanism and rates of cation exchange and binding, e.g. ^{1}H,[59,106] ^{7}Li,[60] ^{23}Na,[61] and ^{39}K[62] n.m.r.

(d) Polarography has recently been used to obtain kinetic and thermodynamic data relating to the 'macrocyclic effect' on the complex (Cu(II) cyclen)[63] where cyclen is 1,4,7,10-tetraazacyclododecane.

A. Cation Size

There is a marked correlation between log K and cation size* for a given ligand cavity diameter. For the two isomers of the ligand dicyclohexyl-18-crown-6, figure 1.2.3 shows the effect on log K of varying the cation radius (and charge).[52] A number of factors are immediately obvious :

(i) For both mono- and bivalent cations a maximum stability is reached for a given cation size.

(ii) The change of log K with cation radius is smaller in the case of the monovalent cations.

(iii) There is extreme selectivity towards certain ions, e.g. the difference in stability constants for Ca^{2+} and Pb^{2+} - dicyclohexyl-18-crown-6 complexes is about 10^{5}.

* Cation ionic radii are generally from Pauling.

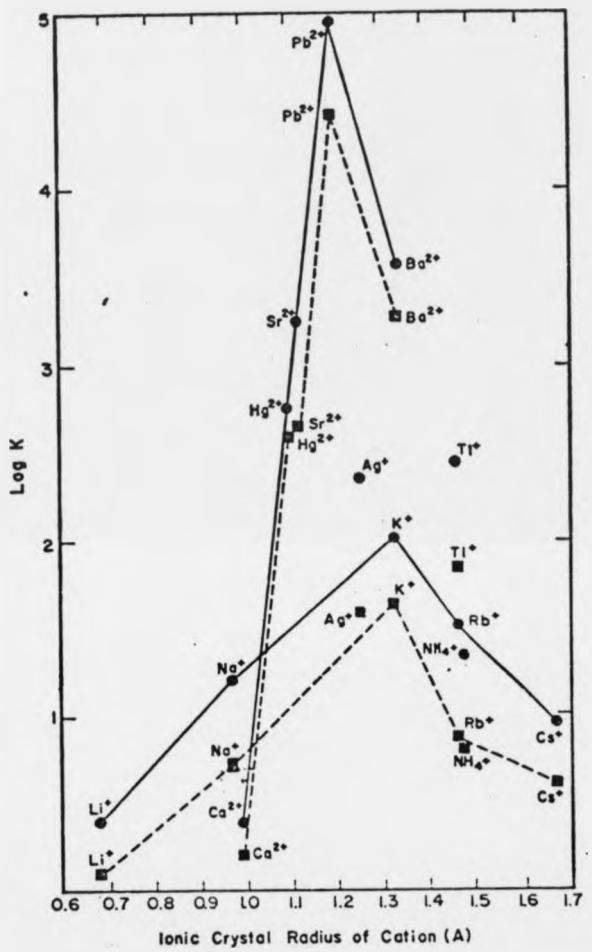


Figure 1.2.3. Plot of log K vs cation radius for the reaction in aqueous solution, $M^{n+} + L = ML^{n+}$ where L = dicyclohexyl-18-crown-6, isomer A (O), and dicyclohexyl-18-crown-6 isomer B (□), T - 25°.

(iv) For cations of approximately the same radius such as K^+ (ionic radius 1.33 Å) and Ba^{2+} (ionic radius 1.35 Å) there is an almost 10^2 increase in K for the doubly charged cation.

It is reasonable that the primary cause for the lower stability of complexes involving cations larger than the optimum size (e.g. Cs^+) is that these cations are too large to "fit" into the ligand cavity. X-ray crystal data* confirms this to be a reasonable belief. Conversely, as the cation size decreases from optimum, the hydration energy of the cation becomes predominant and little or no reaction is found (e.g. Ca^{2+}).

Thermodynamic data is available[52] showing how the values of log K depend upon ΔH^o and ΔS^o values, table 1.2.1. The magnitudes of log K along the series K^+, Rb^+ and Cs^+ are determined predominantly by progressive changes in the ΔH^o values. However, the increase in log K on going from K^+ to Ba^{2+} (which have similar ionic radii) is determined by both ΔH^o and ΔS^o being favourable for the formation of the Ba^{2+} complex.

TABLE 1.2.1

Log K, ΔH^o and ΔS^o data for the reaction $M^{n+} + L = ML^{n+}$, in aqueous solution at 25°, where L = dicyclohexyl-18-crown-6 isomer A, reference 52.

M^{n+}	Log K	ΔH^o Kcal/mole	ΔS^o Kcal/mole	Cation ionic radius Å
K^+	2.02	- 3.88	- 3.8	1.33
Ag^+	2.36	+ 0.07	+ 11.0	1.26
Rb^+	1.52	- 3.33	- 4.2	1.48
Cs^+	0.96	- 2.41	- 3.7	1.66
Tl^+	2.44	- 3.62	- 1.0	1.40
Sr^{2+}	3.24	- 3.68	+ 2.5	1.13
Ba^{2+}	3.57	- 4.92	- 0.2	1.35
Hg^{2+}	2.75	- 0.71	+ 10.2	1.10
Pb^{2+}	5.0	- 5.58	- 3.9	1.20

* See section 1.2.2 F and references therein

B. Cavity Size

Frensdorff[52] has determined log K values for the reaction in MeOH of several cyclic polyethers of varying ring size and numbers of donor atoms with Na^+, K^+ and Cs^+ cations. This data, together with a comparison of cation diameters and estimated ligand 'hole' sizes, is presented in figure 1.2.4. For a given ring size there is a close correspondence between the cation diameter for which maximum stability is found and the compound hole diameter. For example, the maximum log K value for K^+ is reached with cyclohexyl-18-crown-6 and the cation and estimated ligand hole diameters are 2.66 and 2.6 - 3.2Å respectively.

The value of log K drops along the series K^+-18-crown-6, K^+-21-crown-7, K^+-24-crown-8, but surprisingly increases again in the case of the largest ligand complex K^+-dibenzo-30-crown-10. This is partially explained by the observation, based on X-ray crystallography,[98] that the latter ligand is conformationally flexible, and that marked deformation occurs as it 'wraps' around the K^+ cation. This causes an effective reduction of the ligand hole diameter and a corresponding increase in stability.

C. Donor Atom Number and Type

The nature of the binding sites has a clear influence on complex stability. For the alkali metal cations, which are hard Lewis acids, it follows the expected sequence of electrostatic interactions, O > N > S. The data[52] in table 1.2.2 illustrates the effect on log K of progressively replacing the O-donors at the 1,10 positions by N or S in 18-crown-6. For K^+ in MeOH each successive replacement of O by NH causes K to decrease by almost 10^2. Furthermore, substitution of two O by two S atoms causes a 10^5 decrease in stability. For Ag^+, which has significant soft acid character, the sequence of preferred donors is reversed and S >N> O. The stability of Ag^+ complexes in aqueous solution increases as O-donors are replaced by N or S. This then reflects the increased covalent character of the metal-donor atom bond in the Ag^+ complexes of the ligands containing N and S. Similar results have been reported[65] for 15-crown-5 and its sulphur analogues, table 1.2.2. Again, a marked enhancement in stability is observed for Ag^+ when sulphur is substituted for oxygen.

In line with these trends the only reported 'crown' complexes of the later transition metals of group VIII involve ligands containing N or S donors. For example, rhodium(III) complexes of cyclic tetradentate nitrogen ligands such

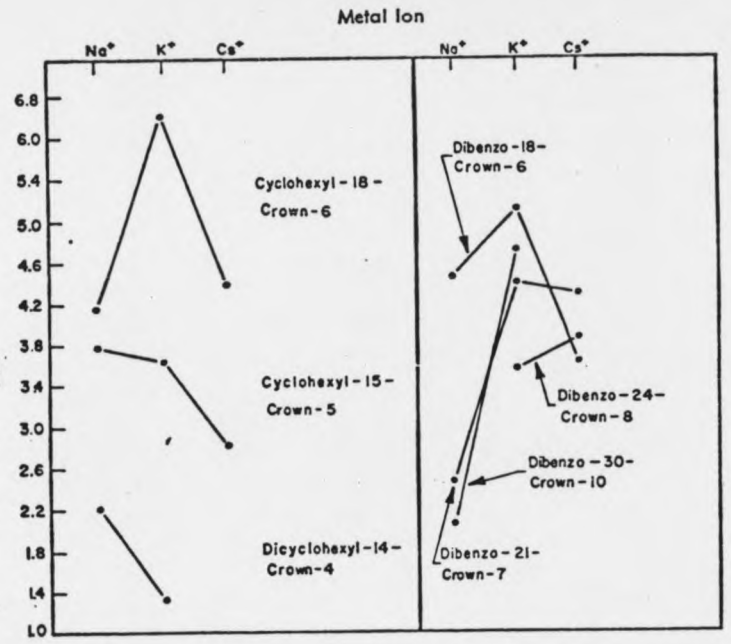


Figure 1.2.4. Log. K values in MeOH at 25 for the reaction of Na^+, K^+, and Cs^+, as chlorides, with a range of cyclic polyethers. $M^+ + L = ML^+$, ref. 52 .

Cation and Hole Diameters, ref. 52

Cation	Cation Diameter (A)	Polyether Ring	Hole Diameter (A)
		14-Crown-4	1.2-1.5
Na^+	1.90	15-Crown-5	1.7-2.2
K^+	2.66	18-Crown-6	2.6-3.2
Cs^+	3.38	21-Crown-7	3.4-4.3

Table 1.2.2.

LogK values for the reaction $M^+ + L = ML^+$, where $L = A(CH_2CH_2.OCH_2CH_2OCH_2CH_2)_2B$, see table 1.2.1. for similar ligands.

A	B	K^{+} b)	Ag^{+} c)
O	O	6.10	1.60
NH	O	3.90	3.3
NH	NH	2.04	7.8
S	S	1.15	4.34

a) Data from ref. 52.
b) Data for MeOH.
c) Data for H_2O.

Log K values for the reaction $M^{n+} + L = ML^{n+}$

M^{n+}	L = 15-crown-5.	L = thia-15-crown-5.
K^+	0.74	a)
Tl^+	1.23	0.80
Ag^+	0.94	5.2
Pb^+	1.85	1.70

a) No measurable reaction. Ref. 53.

as 1,4,7,10-tetraazacyclododecane, cyclen,[66] and 1,4,8,11-tetraazocyclotetradecane, cyclam,[67] and of the tetra-thia analogue[68] of cyclam are known. Some interesting complexes of the polyhetero ligand 1-oxa-7,10-dithia-4,13-diazacyclopentadecane have been reported.[69] X-ray data[70] on a Pd(II) complex of this ligand indicates that the basic geometry is defined by an approximately square planar, N_2S_2, donor set but with a substantial Pd-O interaction causing a marked distortion from square planarity. A study[69] of the stability constant (K) of this ligand shows that it also forms strong complexes with first row transition metals :

TABLE 1.2.3

Log K values for the reaction $M^{2+} + L = ML^{2+}$, in aqueous solution at 25^{o}, where L = 1-oxa-7,10-dithia-4,13-diazacyclopentadecane, reference 69

M^{2+}	log K*
Cu^{2+}	11.6 (1)
Ni^{2+}	7.98(8)
Co^{2+}	5.42(3)
Zn^{2+}	5.09(1)
Pb^{2+}	5.67(3)

* Standard deviations in parentheses

Interestingly it does not complex the alkali metals as do the diaza-polyoxa and macrocyclic polyethers in general. It is clear that macrocyclic ligands containing N or S (or P) donors have an important role to play in the complexation of the later transition metals.[69]

D. Macrocyclic Effect[71-74, 63]

Cabbiness and Margerum[71] define the term 'macrocyclic effect' to describe the enhanced stability of a M^{n+}-macrocyclic chelate complex over that of the corresponding M^{n+}-linear chelate complex. As an example they show for Cu^{2+} complexes of corresponding linear and macrocyclic tetramines, that the

cyclic ligand is ~10^4 more stable (figure 1.2.5). Similarly, Frensdorff[52] has compared log K values of pentaglyme $CH_3(OCH_2CH_2)_5OCH_3$ and 18-crown-6 complexes with Na^+ and K^+ (table 1.2.4). This data shows that the cyclic ligand again results in stabilities some 10^3 - 10^4 higher.

TABLE 1.2.4

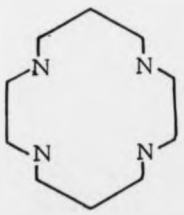
Log K values for the reaction in MeOH at 25° of Na^+ and K^+ with pentaglyme and 18-crown-6, reference 55

Polyether	Na^+	K^+
Pentaglyme [a)]	1.52	2.20
18-crown-6	4.32	6.10

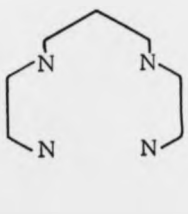
a) $CH_3(OCH_2CH_2)_5OCH_3$

A marked increase in stability is also observed on changing from a monocyclic to a bicyclic ligand (figure 1.2.5). Indeed, the bicyclic amines or cryptates in general result in complexes more stable than the corresponding monocyclic 'crown' complexes.

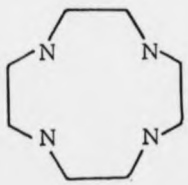
The origin of the macrocyclic effect is not well understood. Recently Hinz and Margerum[72] assigned a ~ 10^7-fold increase in the stability constant of Ni(cyclam)$^{2+}$ compared to Ni(2,3,2-tet)$^{2+}$ to a more favourable change in ΔH which overcomes a less favourable change in ΔS, and reasoned that the free macrocycle is less solvated due to steric hindrance and hence less enthalpic energy need be expended for desolvation before complexation.



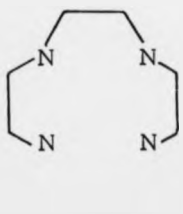
cyclam



2,3,2-tet



cyclen

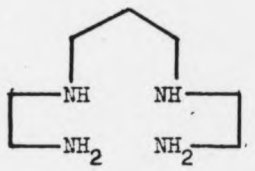


trien

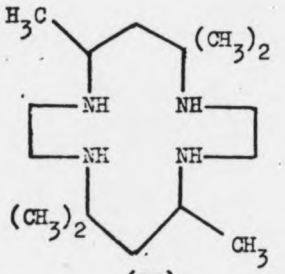
Figure 1.2.5. Some examples illustrating the macrocyclic effect.

Log K values for the formation of several 1:1 Cu^{2+} - tetramine complexes at 25° in aqueous solution, ref. 71.

Ligand	Log K
(I)	23.9
(II)	28



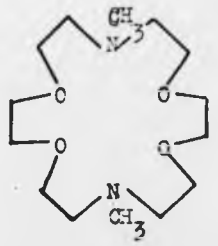
(I)



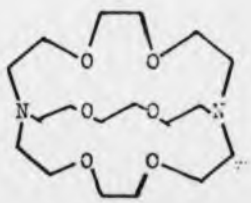
(II)

Log K values for the formation of K^+ complexes of mono- and bi-cyclic crown ligands, at 25° in methanol/water, 95/5, ref. B. Dietrich, J. Lehn, J. Sauvage, J.C.S. Chem. Comm., 1973, 15.

Ligand	Log K
(III)	4.4
(IV)	9.45



(III)



(IV)

They further argued that a difference of two in the number of ligand solvating H_2O molecules accounts for the difference in ΔH between the cyclam and 2,3,2-tet reactions but that the difference in ΔS values for the two reactions (16 cal $^oK^{-1}$ mole^{-1}) was less than would be predicted for the release of two H_2O molecules (see table 1.2.5); this was attributed to the greater loss of configurational entropy, on complexation, for the open chain ligand.

TABLE 1.2.5

Complex	log K_{ML}	ΔH Kcal/mole^{-1}	ΔS cal $^oK^{-1}$ mole^{-1}
Cu (cyclen)$^{2+}$ a)	24.8	- 18.3	51.4
Cu (trien)$^{2+}$ b)	20.0	- 21.6	19.5
Cu (2,3,2-tet)$^{2+}$ b)	23.9	- 27.7	16.5
Ni (cyclam)$^{2+}$ c)	22.2	- 31.0	- 2
Ni (trien)$^{2+}$ c)	13.8	- 14.0	16.0
Ni (2,3,2-tet)$^{2+}$ c,d)	15.4	- 16.8	14.0

a) ref. 63, b) ref. 73, c) ref.72. Data on aqueous solutions at 25^o. d) data for the square planar complex.

In marked contrast polarographic studies[63] on Cu(II) cyclen complexation have shown that the thermodynamic and kinetic macrocyclic effect is evident despite the unfavourable steric constraint of the 12-membered ligand ring. The increased stability of the Cu(II) cyclen complex when compared to Cu(II) trien is accounted for solely by the entropy term. As the authors note[63] the contrast in thermodynamic parameters between Cu (cyclen)$^{2+}$ and Ni (cyclam)$^{2+}$ does not seem fully accountable by the difference in the metal ion or the ligand ring size. The 'macrocyclic effect' may depend upon factors such as configurational entropy, entropy of solvation, enthalpy of solvation and enthalpy of metal-ligand bond formation. Until the relative importance of these terms for the free and complexed, linear and cyclic ligands is determined, the origin of the macrocyclic effect will remain uncertain.

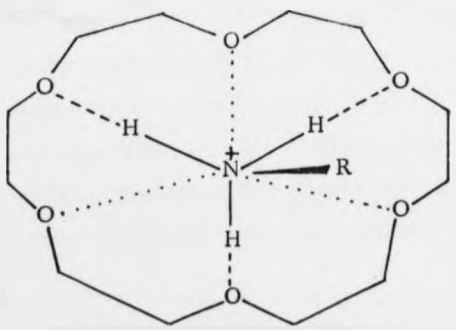
E. Complexation of Organic Substrates

The formation of crown ether-metal cation inclusion complexes may formally be considered as a molecular recognition[75] process in which association of two chemical species is controlled by information stored in the ligand and substrate. The recognition of spherical substrates, the alkali cations, by synthetic macrocyclic ligands has been described in this section. The design of ligands capable of complexing non-spherical organic molecules is a topic of current interest. One kind of naturally occurring compound, the cyclodextrins, are known to form well defined inclusion complexes with a variety of organic substrates.[76]

Early work described the synthesis and organic molecular recognition properties of macrotricyclic cryptates.[77] Cram demonstrated that 18-crown-6 formed inclusion complexes with a variety of arene diazonium salts, in which the linear $Ar-N\equiv N^{+}$ moiety is thought to insert into the hole of the crown with O-donors directed towards the charged nitrogens.[78] Very recently Cram has begun a systematic study of the parameters that control association constants between polyether hosts and alkylammonium guest compounds,[79] e.g.

$$[\text{Host}] + [(CH_3)_3C\overset{+}{N}H_3 \cdot SCN^{-}] \underset{CHCl_3}{\overset{K}{\rightleftharpoons}} [(CH_3)_3C\overset{+}{N}H_3 \cdot \text{Host} \cdot SCN^{-}]$$

Here the best hosts studied were 18 membered derivatives of 18-crown-6 in which $-(CH_2)_2O(CH_2)_2-$ groups were substituted for 1,3-benzenedimethylyl, 2,5-furandimethylyl or 2,6-pyridinedimethylyl groups. 18-crown-6 has an almost optimum arrangement of donor atoms for complexing the amine studied ($K = 7.5 \times 10^5$). Although crystallographic data is not available, it appears that the trigonal disposition of 3 hydrogen bonds between ligand O and substrate and three trigonal $O \cdots\cdots \overset{+}{N}$ interactions is critical to strong binding, see below :

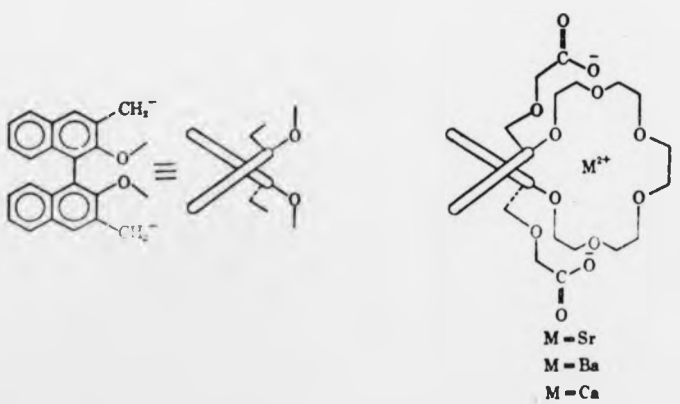


More recently Cram has shown[80] that macrocyclic polyethers incorporating the 1,3-xylyl group* can direct functional units attached in the 2-position towards the centre of the ligand. These inwardly directed groups (e.g. carbonyl or carbomethoxy) can act as additional binding sites for alkylammonium anionic guests. Whilst it is observed that these groups probably destabilise the complexes (relative to a complex unsubstituted in the 2-position), their potential as catalytic sites is under investigation.

'Chirospecific' molecular receptors are known. Both optically active macrocyclic amino-ethers[81] and polyethers have been described. The latter work by Cram demonstrated how the 1,1'-binapthyl group may be incorporated into cyclic polyethers providing host compounds with chiral recognition in complexation of primary amines,[82] amino acids[83] and amino esters.[84] This group was also shown to allow for the attachment of arms terminating in functional groups,[83,85] that extended around over or under the central cavity of the cycles. In the latter context the paracyclophanyl group is also reported[86] to be valuable as a structural unit.

Binapthyl substituted crown ethers with pendant groups are particularly interesting since Cram has demonstrated that they will complex metal ions as well as amino acid substrates. For example,[83] the derivative of 18-crown-6 shown in figure 1.2.6 forms stable 1:1 complexes with Sr, Ba or Ca.

FIGURE 1.2.6



reference 83

* See also reference 106

The two pendant carbonyl groups are believed to lie above and below the metal cation as shown, acting as 'built in' counterions. Unfortunately the thermodynamic effects of introducing 'built in' counterions have not yet been studied, but stable 1 :1 complexes are formed only when the number of counterions equals the number of positive charges on the cation.

Cram's most recent work has shown that it is now practical to design host compounds for optically resolving amino esters.[84] Furthermore, other workers have recently extended Cram's work by preparing chiral-binapthyl derivatives of the macrobicyclic amines (cryptates).[87]

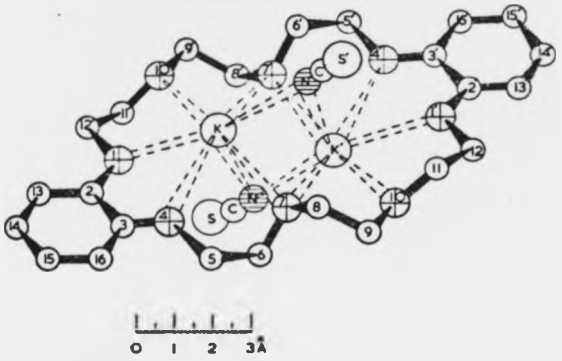
F. Structural Studies

X-ray crystallographic studies have proved valuable in corroborating the results of the thermodynamic studies summarised in the previous sections. Dunitz et al.[88,95,96] and Truter[89,97] have carried out particularly extensive studies on crown ether complexes with a variety of metal ions, whilst Louis, Metz and Weiss[90,99-104] have reported many structures of bicyclic cryptate metal complexes and more recently of metal complexes of mixed O, N and S-donor crown analogues.[105,70]

In general polyether macrocycles tend to form complexes with alkali metal salts in which the metal is held in (or close to) the centre of a ring of approximately coplanar oxygen donors. For small rings containing 5 or 6 oxygen atoms, 1 :1 complexes are formed between polyether macrocycles and alkali metal ions, only when the ligand cavity and metal ion sizes are comparable. In addition, coordination of additional molecules of H_2O to the metal ion either from above or below the plane of the ligand ring is often encountered.[91] For example, benzo-15-crown-5 (estimated cavity size 1.7 - 2.2 Å) forms a 1 :1 complex with NaI, namely (benzo-15-crown-5)(NaI)(H_2O),[92] (cation diameter sodium = 1.90 Å) but a 2 :1 (ligand : metal) complex with KI in which the larger K^+ cation (cation diameter = 2.66 Å) lies on a centre of symmetry between two ligand planes, separated by 3.34 Å, with the O-donors of the two ligands forming a pentagonal bipyramidal antiprism donor set.[93] Similar behaviour is noted for alkali-metal complexes of 18-crown-6 and its substituted derivatives,[88,94] although here a large number of thiocyanate salts have been investigated in which the SCN anion either functions as a donor to the metal[95] or as a bridging

ligand giving dimeric units.[96] Larger rings are capable of complexing two metal ions, for example dibenzo-24-crown-8 forms the 1 :2 complex (dibenzo- 24-crown-8)$(KNCS)_2$:[97]

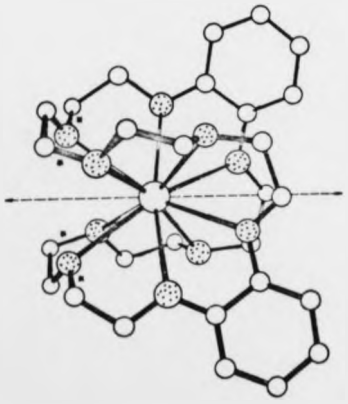
FIGURE 1.2.7



One molecule of the 2:1 complex of potassium thiocyanate with dibenzo-24-crown-8

Here sharing of thiocyanate and ligand O-donors allows each K cation to be surrounded by 5 oxygens in a plane with nitrogens above and below this plane, together with interactions with carbon atoms of a benzene ring in an adjacent unit cell. As the ring gets even larger the macrocycle tends to form 1 :1 complexes in which the ligand ceases to be essentially planar and wraps around the metal cation. For example, dibenzo-30-crown-10 forms a 1 :1 complex with KI in which the cation is completely enclosed in a 3D-cavity with all 10 oxygens donating to it:[98]

FIGURE 1.2.8

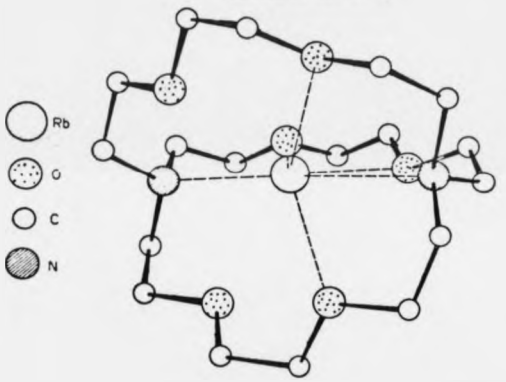


The potassium (dibenzo-30-crown-10) complex in KI (*XX*). Asterisks mark the bonds which have different torsion angles in the uncomplexed molecule

The resemblance to the naturally occurring K^+-nonactin complex and its relevance to ion transport phenomena has been noted.[89] Recently Mallinson[94] has begun a study of the effect of introducing small structural changes and is investigating how the various isomers of tetramethyl-dibenzo-18-crown-6 differ in their complexing abilities.

Polyoxa macrobicyclic amines form another large groups of compounds which have been studied by crystallography. Metz, Moras and Weiss have determined the crystal structures of the 1 :1 complexes formed by [2,2,2] cryptate and the metal ions, Na^+, K^+, Rb^+, Cs^+, Tl^+, Ca^{2+}, Ba^{2+} (and the free ligand).[90]

FIGURE 1.2.9



The complex cation of (Rb)(SCN)(2,2,2-cyptate)(H_2O)

Here the cations are shown to lie roughly centrally in the ligand cavity being coordinated both to the 2 nitrogen and 4 oxygen donors. Comparison of these structures with that of the uncomplexed ligands shows that there are conformational changes mainly in the $-CH_2OCH_2CH_2-$ torsion angles but there is no inversion at nitrogen which remains in the lone pair 'in-in' configuration. There appears to be some correlation between the metal-oxygen and metal-nitrogen bond lengths, ligand cavity size and stability constants (table 1.2.6).

For example, the order of stabilities $K^+ > Rb^+ > Na^+ >> Cs^+$ reflects the fact that sodium is too small and caesium is too large to fit the ligand cavity.

TABLE 1.2.6

Some complexes of [2,2,2]-cryptate (L):

Complex	log K [a]	M-O [b]	M-N [b]	Ionic diameter of cation [c]	Reference to crystal structure
NaI.L	3.9	2.57	2.77	1.9	99
KI.L	5.4	2.79	2.87	2.66	100
Rb(SCN)(H_2O).L	4.35	2.90	3.00	2.96	101
Cs(SCN)(H_2O).L	<2	2.97	3.03	3.38	101
Ca(Br_2)(3·H_2O).L	4.4	2.52	2.72	1.98	104
Ba$(SCN)_2$(H_2O).L	9.5	2.78	2.96	2.70	102
Tl(H·COO)(H_2O)·L	6.3	2.91	2.90	2.80	103

a) log K values in aqueous solution at 25° from reference 89.

b) Average values in Å

c) The estimated ligand cavity diameter of [2,2,2]-cryptate is 2.8 Å, reference 89.

G. Conclusion

As mentioned in the introduction to this section, a part of the work described in this thesis involved the attempted preparation of macrocyclic phosphino-ethers. From the preceding discussions on the stability of group VIII transition metal bonds with phosphorus ligands (section 1.1), and the properties of crown ethers, a number of broad conclusions may be drawn about the properties of such ligands :

(i) Providing factors such as cavity and cation size remain compatible, the introduction of softer donors such as N, S (or P) will favour the complexation of softer metal cations as predicted by the HSAB theory.

(ii) Covalent bonding character increases with the use of softer donors and acceptors.

(iii) An increase in stability is often observed for complexes having appreciable covalent character.

(iv) Transition metal bonds typically have specific directional properties, involving the use of specific orbitals. Typical coordination geometries for transition metals (e.g. planar) are different from those predicted on purely electrostatic considerations. It is therefore likely that the arrangement of soft donors will have a greater effect on complex stability than that of hard donors.

It is clear that the introduction of soft donors such as phosphorus may be used to discriminate strongly against hard cations such as the alkali metals whilst favouring group VIII cations. Furthermore, judicious variation of the parameters affecting complexation, such as cavity size and number and dispostion of hard and soft donors, may eventually allow macrocyclic ligands to be 'tuned' to enhance either the stability or selectivity for complexes with a wide range of metal cations.

SECTION 1.3

The Chemistry and Catalytic Properties of Group VIII b Organometallic Compounds

Introduction

Chemists have found it useful to organise organic chemistry into patterns of mechanistically related transformations. In recent years analogous patterns have been found and investigated for organo-transition metal compounds. A useful basis for such discussion is the concept of formal electronic configuration, oxidation state and coordination number at the central metal atom.[111] This is necessarily imprecise, involving as it does a valence-bond formalism. Despite this such correlations provide a useful framework within which the basic reactions of organometallic systems may be organised and discussed.

Much interest has been shown in the application of organometallic compounds to homogeneous catalysis. Such reactions involving the concepts of coordinative unsaturation,[111] oxidative addition, insertion, the stabilisation of reactive intermediates and the activation of substrates, illustrate many of the most important features of organometallic chemistry. It is therefore convenient to briefly discuss the chemistry of the group VIII b transition metals in this context.

1.3.1 Coordinative Unsaturation

The transfer of atoms or groups of atoms from a metal atom to a ligand or vice versa is one of the fundamental processes involved in catalysis. Accordingly, a vacant coordination site is perhaps one of the single most important properties of an homogeneous catalyst.[111] Latent coordination sites are not only necessary to activate a substrate by bringing it into the metal coordination sphere, but coordinatively unsaturated complexes are especially reactive in insertion (or migration)[112, 113] and oxidative addition reactions[114] (discussed in subsequent sections). Coordinatively unsaturated species may arise in a number of ways :

(i) They may exist as intrinsically stable species such as square planar d^8 compounds. However, even here solvent molecules may sometimes occupy the remaining sites and will need to be displaced. Also it is known that phosphines

$$ML_4(S)_2 + A + B \longrightarrow ML_4AB + 2S$$

solvated species d^8 coordinatively saturated d^6

and carbonyls can act as antagonists in both heterogeneous and homogeneous catalysis, which can be understood in terms of saturation of essential coordination sites.

(ii) In some complexes active in catalysis, no detectable dissociation occurs. Thus, addition of hydrogen to tristriphenylphosphine rhodium chloride gives an addition complex whose ^{31}P n.m.r. spectrum demonstrated the absence of appreciable dissociation * [115]

$$Rh^{I}Cl(PPh_3)_3 + H_2 \xrightleftharpoons{H_2} Rh(Cl)(H)(H)(PPh_3)_3$$

Phosphine trans to hydride is shown to dissociate readily by observation of selective line-broadening and collapse on addition of free triphenylphosphine. Thus, a five coordinate 16-electron intermediate is formed and is reasonably assumed to be an intermediate in catalysis.

It is noteworthy that the Ir analogue, in which the phosphine ligands are more firmly bound, [116, 117] is not an active hydrogenation catalyst, [111] even though it readily adds hydrogen.

1.3.2 The Oxidative Addition Reaction [111, 114, 118]

When a complex behaves simultaneously as Lewis acid and Lewis base, the so-called oxidative addition reaction results :

$$L_yM^{n+} + XY \longrightarrow L_yM^{n+2}(X)(Y)$$

For such a reaction to proceed there must be :

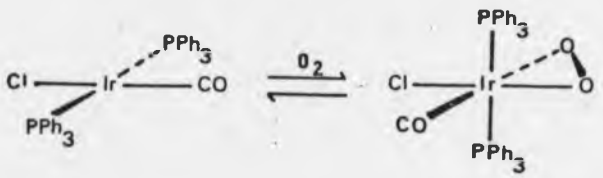
(i) Non-bonding electron density on the metal M.

(ii) At least two vacant coordination sites.

(iii) A metal M with allowable oxidation states separated by two units.

* See also reference 119 and references therein which require re-interpretation in the light of reference 115.

For transition metals the most extensively studied reactions are those of metals with d^8 and d^{10} electron configurations, e.g. Fe^o, Ru^o, Os^o, Rh^I, Ir^I, Ni^o, Pd^o, Pt^o and Pd^{II} and Pt^{II}. Coordinatively unsaturated d^8 complexes are known to add molecules such as protonic acids[120,127], alkyl halides[120, 126, 134], acyl halides[120], metal halides[121], halogens[122], hydrogen[123, 124], oxygen[124, 128], acetylenes[125] and olefins[126] reversibly. Molecules that contain multiple bonds may be added oxidatively without cleavage to form new complexes which have three-membered rings[124, 128], e.g.



Alternatively, five coordinate d^8 complexes can react through dissociation of a ligand prior to oxidative addition[129], e.g.

$$Ru^o(CO)_3(PPh_3)_2 + I_2 \xrightarrow{-CO} Ru^{II}I_2(CO)_2(PPh_3)_2$$

$$Mo^o(CO)_4\,bipy + HgCl_2 \xrightarrow{-CO} Mo^{II}(CO)_3\,bipy\,Cl(HgCl)$$

When no ligand loss is involved, there will be an equilibrium reaction. The square planar complex <u>trans</u>-$IrCl(CO)(PPh_3)_2$ has been particularly well studied[119], e.g.

$$\underline{trans}\text{-}Ir^{I}Cl(CO)(PPh_3)_2 + HCl \rightleftharpoons Ir^{III}HCl_2(CO)(PPh_3)_2$$

The position of the equilibrium depends upon a number of factors :

(i) The nature of the metal and its ligands.

(ii) The nature of the addend, XY, and of the M - X and M - Y bonds so formed.

(iii) The medium in which the reaction is conducted.

Vaska[118] has considered these factors in some detail. The higher oxidation states are usually more stable for the heavier metals so that Ir^{III} species are

generally more stable than Rh^{III} species.[111] For the ligands, factors that tend to increase the electron density on the metal, tend to increase its oxidative reactivity. This may be illustrated by considering hydrogen, a reagent which adds only to the most active d^8 complexes. Whereas bis(1,2-bis(diphenylphosphino)-ethane) iridium cation readily adds hydrogen,[124] the rhodium analogue does not; however, the similar bis(1,2-bis(dimethylphosphino)-ethane) rhodium complex does add hydrogen.[130] Furthermore, in the reactions of square iridium(I) complexes with carboxylic acids, e.g. trans-$IrX(CO)L_2$ + $RCOOH \rightleftharpoons Ir^{III}HX(O_2CR)(CO)L_2$ the equilibria lie further to the Ir^{III} side in the order X = Cl, Br, I and in the order $L = PPh_3 < PMePh_2 < PMe_2Ph < PMe_3$.[127]

These reversible additions often occur in a stereospecific manner; both cis[124] and trans[120,135] modes of addition have been observed, depending upon the reaction and medium. The similarity to chemisorption at a transition metal surface is apparent. Thus, it is not surprising that such additions are often key steps in hydrogenation,[123*] hydroformylation[132] and olefin dimerisation or isomerisation.[133]

The mechanism of oxidative addition reactions are not simple. It has been reported that the addition of alkyl halides to square planar Ir(I) complexes may take place with inversion, retention or racemisation at the alkyl centre and three general mechanisms have been proposed to explain these observations :

(i) An S_n2 process in which Ir(I) acts as a nucleophile[136,126]

(ii) A concerted three centre addition[137]

(iii) A free radical process[138,139]

Similar oxidative additions of alkyl halides to d^8 cobalt have been reported to occur with inversion of configuration at carbon[140] and the addition of silicon hydrides to d^8 and d^{10} platinum or d^8 iridium and cobalt complexes is observed to take place with retention of configuration.[141]

Kinetic studies have shown that the addition of CH_3I or $C_6H_5CH_2Cl$ to trans-$Ir(Cl)(CO)(PPh_3)_2$ or $Pt(PPh_3)_3$ involve an S_n2 type mechanism[136] In contrast, in the presence of small quantities of oxygen or other adventitious radical

* Recently the use of polymer bound complexes of Rh, Ni or Ru for homogeneous catalysis has been extensively investigated. See for example reference 148 and references therein.

initiating impurities, the addition of alkyl halides such as cis or trans-1-bromo-2-fluoro-cyclohexane or 1-bromo-2-phenyl-ethane, to trans-Ir(Cl)(CO)$(PMe_3)_2$ is thought to possibly occur by a radical chain process of the type shown :[138]

$$Ir(I) + Q^{\cdot} \longrightarrow Ir(II) - Q$$

$$Ir(II) - Q + RBr \longrightarrow Br - Ir(III) - Q + R^{\cdot}$$

$$Ir(I) + R^{\cdot} \longrightarrow Ir(II) - R$$

$$Ir(II) - R + RBr \longrightarrow Br - Ir(III) - R + R^{\cdot}$$

where $Q^{\cdot}$ = initiator and the metal oxidation states are used loosely as 'electron book keeping devices'

Similarly in the addition of α-bromo-esters to trans-Ir(Cl)(CO)$(L)_2$, (where L = PMe_3, PMe_2Ph or $PMePh_2$) the rate of addition was strongly inhibited by the introduction of radical scavengers.[139] Using an optically active ester, (RS,SR)-$C_6H_5 \cdot CHF \cdot CHBr \cdot COOC_2H_5$, loss of stereochemistry was observed confirming a free radical pathway to be reasonable.*[139] In this context α-bromo-esters are also observed to give racemic adducts with $Pd(RNC)_2$.[142]

With these studies as a base, Osborn and Kramer have recently shown that a major (but not sole) pathway for the addition of alkyl halides to low valent metal complexes such as $M(PEt_3)_3$ (M = Pt or Pd) involves a radical chain,[143] or in the case of very reactive halides, a radical non-chain process.[144] For the general oxidative addition of an alkyl halide to $M(PEt_3)_3$ (M = Pt or Pd) a mixture of products may occur :[143,144]

$$M(PEt_3)_3 + R \cdot X \longrightarrow M(PEt_3)_2(R)(Br)$$

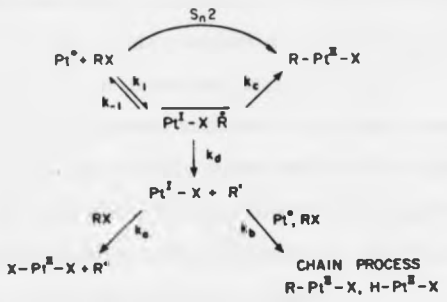
$$M(PEt_3)_2(Br)(Br)$$

$$M(PEt_3)_2(H)(Br)$$

To explain the occurrence of unexpected dibromo and hydrido products, the time dependence of the product ratio, the inhibition sometimes caused by radical scavengers, a racemic mixture of products, and the observation of CIDNP effects

* An earlier study[137] in which optically active $CH_3CH\,Br{\cdot}COOC_2H_5$ was reported to add to trans-Ir(Cl)(CO)$(PMePh_2)_2$ with complete retention of configuration appears suspect in view of reference 139.

(in certain cases), a complex general mechanism is proposed :[144]



Initially two paths are available :

1. S_n2 displacement on carbon may give an incipient cationic complex (possibly strongly ion paired) followed by re-entry of the anion to give the regular oxidative addition product. Recent work by Stille[145] on the addition of benzyl-α-d-chloride to Pd(O) complexes provides strong support for this non-radical route.

2. Halide abstraction may occur (possibly preceded by electron transfer) to form the radical pair, (Pt(I) - X + R$^{\cdot}$). This pair could collapse to give the regular adduct or diffusively separate to form(Pt(I) - X) and (R$^{\cdot}$). Two pathways then develop depending upon the ease with which radicals may be abstracted from RX :

2(i). For very reactive halides such as C_2H_5I or benzyl bromide, (Pt(I) - X) can rapidly abstract further halide (X$^{\cdot}$) to give the dihalide and an organic radical. This agrees with experimental observation and nicely explains the observation of CIDNP effects arising from the diffusive encounter of the product radicals. Furthermore, non-chain radical mechanisms have been invoked to explain the addition of CH_3I, $C_6H_5CH_2Br$ and C_2H_5I to $Pt(PPh_3)_3$, based on trapping experiments using t-BuNO.[146]

2(ii). Less reactive halides such as 1-bromo-butane or neopentyl bromide, which do not facilitate radical abstraction, may react by a complex radical-chain pathway,[143] which is initiated by the organic free radicals.

This leads to the regular adduct and/or hydrido adducts and ultimately to the dibromo adduct. This explains the observation that whilst prolonged reaction gives substantially the dibromo adduct, the initial reaction mixtures contain large proportions of the regular adduct and hydrido adduct. Reactions of this type were the subject of an extensive earlier study.[143]

It is clear that oxidative addition to the later transition metals may be far more complex than previously suspected and for a given system will depend upon the nature of the carbon-halogen linkage, the nucleophilicity of the metal complex, the ability of the metal complexes to undergo one-electron processes, as well as steric and ligand exchange effects.

Very recently Kochi and others have shown[147] that one-electron transfers have wide applicability in the general field of organometallic intermediates. Much interesting work is expected in this area in the future.

1.3.3 Migration of Atoms or Groups from Metal to Ligand : the "Insertion Reaction"

The concept of 'insertion'[149,150] is of wide applicability when defined as a reaction in which any atom or group of atoms is inserted between two atoms initially bound together.

$$L_nM - X + YZ \longrightarrow L_nM - (YZ) - X$$

Some general examples are :

$$Ti(NR_2)_4 + 4CS_2 \longrightarrow Ti(S_2CNR_2)_4$$

$$R_3PbR' + SO_2 \longrightarrow R_3PbOS(O)R'$$

$$(CO)_5MnCH_3 \xrightarrow{CO} (CO)_5MnCO \cdot CH_3$$

For transition metals the most detailed studies have been made on the 'insertion' of CO into metal-alkyl bonds. Mechanistic studies have been made using $CH_3Mn(CO)_5$ or related compounds.[113] With ^{14}CO as tracer, it has been shown that :

(i) The CO molecule that undergoes insertion into the metal-alkyl bond is already coordinated to the metal atom

$$CH_3Mn(CO)_5 + {}^{14}CO \longrightarrow CH_3CO\,Mn(CO)_4({}^{14}CO).$$

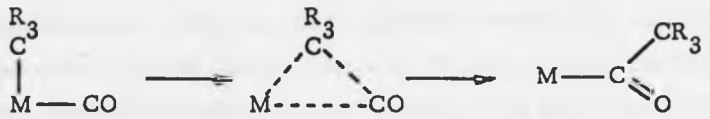
(ii) The incoming CO adds cis to the acyl group.

(iii) The insertion is promoted by alternative ligands such as PPh_3, e.g. $CH_3Mn(CO)_5 + PPh_3 \longrightarrow CH_3CO\,Mn(CO)_4(PPh_3)$.

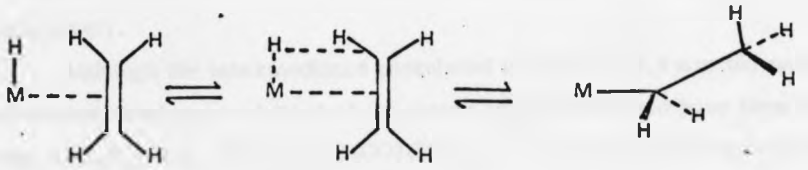
Kinetic studies have shown that the first step involves an equilibration between the octahedral alkyl and five coordinate species, e.g.

$$CH_3Mn(CO)_5 \rightleftharpoons CH_3CO\,Mn(CO)_4$$

The incoming ligand then adds to the five coordinate species. The insertion reaction might therefore be considered as an alkyl migration to a coordinated CO molecule in a cis position, possibly proceeding via a three centre transition state.



More complicated transition states may be involved in the important hydride transfer to alkenes to form alkyls in catalytic hydrogenation.[151]



1.3.4 Hydroformylation of Alkenes[132,152-155]

The features of coordinative unsaturation, oxidative addition and insertion discussed in the preceding sections are all important aspects of the catalytic hydroformylation of alkenes. Accordingly, this is taken as a final example of the chemistry of group VIII b metals.

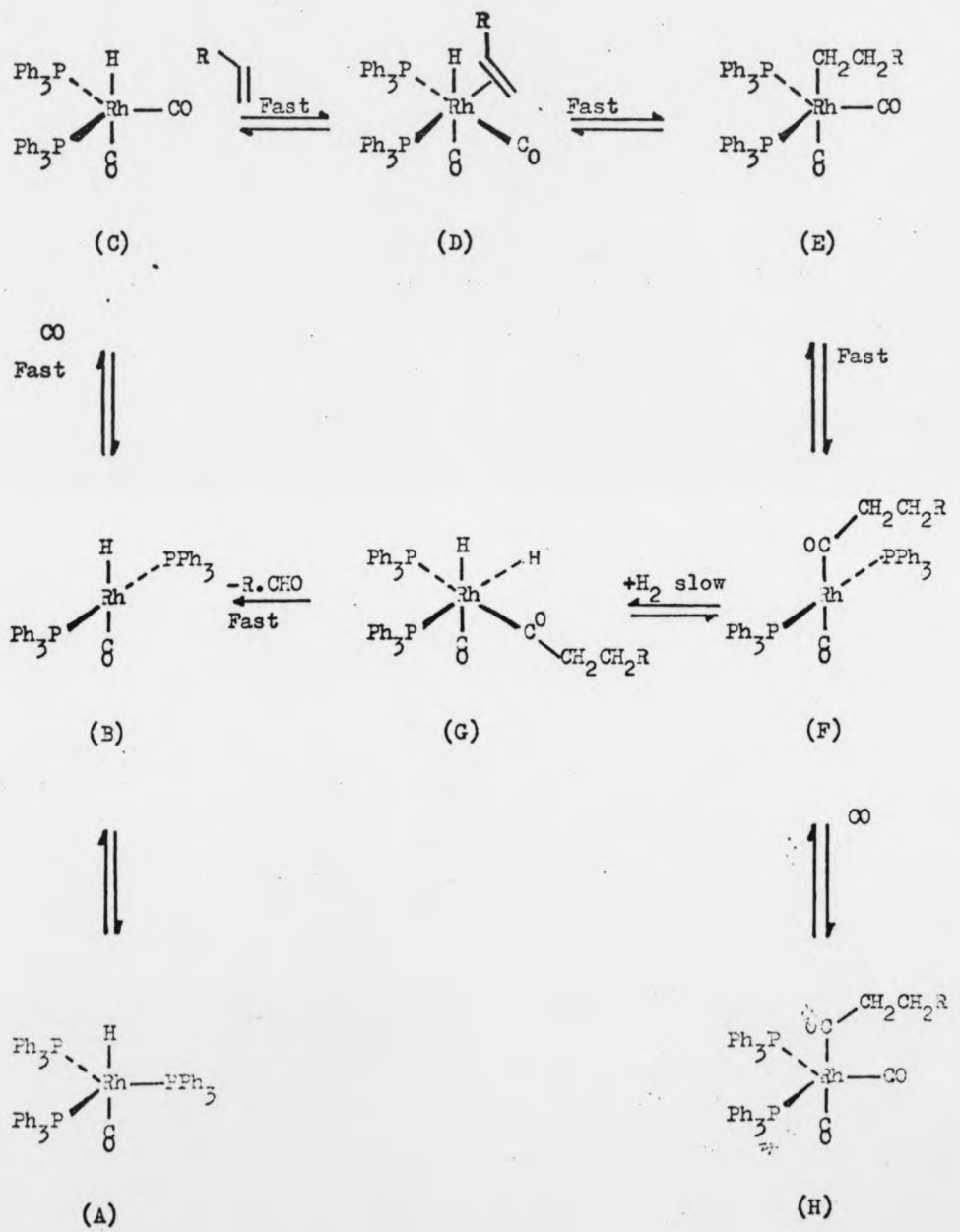
The major features of the hydroformylation reaction in which H_2 and CO are added to an alkene to form an aldehyde were mainly elucidated by Orchin, Heck and Breslow through studies on the reaction of the hydridocarbonyl, $HCo(CO)_4$, with olefins.[156] A more convenient catalyst for study is $RhH(CO)(PPh_3)_3$ which is catalytically active even at 25° and 1 A.P. pressure.[152] In contrast to the Co system this catalyst gives largely linear aldehydes, especially in the presence of high PPh_3 concentrations (or better if molten PPh_3 is used as the solvent). A proposed reaction cycle is shown in figure 1.3.1.

Thermal dissociation of PPh_3 leads to a square planar intermediate (B) which reversibly adds CO to form the active species $RhH(CO)_2(PPh_3)_2$, (C). Associative attack of the alkene on (C) and subsequent hydride migration, affords the anti-Markownikoff alkyl (E), which undergoes CO insertion to form the four coordinate acyl derivative, (F). The latter complex undergoes oxidative addition of molecular hydrogen to afford the dihydroacyl complex, (G). This step involves a change in oxidation state and may be rate-determining. The final steps are hydride migration to the carbon atom of the acyl group, resulting in reductive elimination of aldehyde and regeneration of the four coordinate species, (B).

An excess of CO, over H_2, is known to inhibit the reaction, probably through formation of five coordinate dicarbonyl acyls, (H), which cannot add H_2. Furthermore, the high concentrations of PPh_3 necessary to produce high yields of linear aldehyde probably function by suppressing the dissociative formation of monophosphine species such as $RhH(CO)_2(PPh_3)$. In such four coordinate species there is little specificity between anti-Markownikoff and Markownikoff addition of alkenes, which leads to the formation of both linear and branched aldehydes respectively.

Although the intermediates postulated in figure 1.3.1 are too unstable to be isolated, analogues of most of the major species involved have been isolated using (i) C_2F_4, e.g. $Rh(C_2F_4H)(CO)(PPh_3)_2$[157] and (ii) more stable iridium complexes derived from $IrH(CO)_2(PPh_3)_2$.

Figure 1.3.1. Catalytic cycle for the hydroformylation of alkenes using $RhH(CO)(PPh_3)_3$, ref. 152 .



SECTION 1.4

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CHAPTER 2

CHAPTER 2

Synthesis of Phosphino-Ethers

2.1 Introduction

Potential synthetic routes to mixed phosphorus/oxygen crown ether analogues have been investigated. Synthesis of such compounds has not yet been achieved, but a number of linear relatives have been produced in very good yield. These relatives have been shown to exhibit some of the complexing properties expected for the macrocyclic systems.

Methods for the Synthesis of Phosphorus-Carbon Bonds

There are many reported methods[1] for forming phosphorus-carbon bonds and a large number of phosphorus containing ligands are reviewed in the literature[2]. Despite this there are few flexible synthetic methods available and these involve air sensitive, toxic and malodourous organophosphorus compounds. These factors together with the inherent difficulties of macrocycle synthesis have meant that macrocyclic diphosphines have only recently been reported[3]. Two synthetic methods of some generality are discussed: the first (A) is used in this work and the second (B) has been successfully used to synthesise the macrocyclic diphosphines reported by T.H. Chan and B.S. Ong[3].

A. Reactions involving Alkali-Metal Phosphides

The Basicity and Nucleophilicity of Phosphines:

Beauchamp has recently reported an important study of the basicities of the methyl phosphines in the gas phase, by ion-cyclotron resonance[4]. The results are compared with gas phase studies on amines and with solution basicities. Selected data is given in Table 2.1.

Table 2.1

The solution and gas phase basicities of phosphines and amines

Molecule	Gas phase proton affinity[a] in Kcal/mole.	Solution[b] pKa
PH_3	187.9	-14
$MePH_2$	206.9	~0
Me_2PH	218.9	3.91
Me_3P	228.0	8.67
NH_3	207.0	9.1
$MeNH_2$	216.3	10.62
Me_2NH	224.4	10.64
Me_3N	226.6	9.76

a) Reference 4

b) Reference 9

In the methylamine series, beginning with NH_3, successive increases in gas phase proton affinity of 9.3, 6.1, and 4.2 Kcal/mole are observed for substitution of the first, second and third methyl groups. In solution this systematic behaviour is largely cancelled by an opposite systematic effect of methyl substitution, namely loss of specific strong hydrogen bonds between solvent molecules and acidic hydrogen (protonic binding sites) in BH^+ ($B=NH_3$, NH_2Me, $NHMe_2$ and NMe_3)[4,5]. The analagous increments in proton affinity for the methyl phosphines are 19.0, 12.0, and 9.1 Kcal/mole, with increasing methyl substitution. Methyl substituent effects in the phosphine series are about twice as large as in the amine series, thus whilst PH_3 is a weaker base than NH_3 the order is reversed for Me_3P and Me_3N (in the gas phase).

Beauchamp gives a qualitative explanation of these differences in the gas phase basicity by considering the character of the lone pair to which the proton binds in these series[4]. For NH_3, sp^3 hybridisation is a reasonable description of the lone pair orbital. Weaver and Parry have summarised evidence which suggests that the largest contribution to the dipole moments of amines can be assigned to the lone pair. In proceeding from NH_3 to NMe_3 the dipole moment decreases from 1.47 to 0.61D which in terms of hybridisation concepts implies that methyl substitution progressively introduces more s character into the lone pair orbital[6]. Protonation of the methylamines is thus accompanied by a rehybridisation energy which increases with methyl substitution. This acts in opposition to the stabilisation afforded by interaction of the charge on nitrogen with the polarisable methyl groups.

In contrast ab initio calculations by Guest, Hillier and Saunders suggest that the lone pair orbital of both PH_3 and Me_3P can be described as $sp^{0.8}$ and that no rehybridisation accompanies methyl substitution[7]. Thus in the phosphine series rehybridisation energy is significant but does not change greatly with methyl substitution. This appears to lend greater stabilisation to the conjugate acids than is observed in the amine series. Another possible origin of the larger methyl substituent effect of phosphines could involve donation from π-type orbitals of the CH_3 group into empty phosphorus dπ orbitals.

Beauchamp has also compared solution and gas phase data[4]. Using the data of Arnett[8], for the heats of protonation of PH_3 and Me_3P in HSO_3F in conjunction with the gas phase data, the differences in enthalpies of solvation for the conjugate acids were calculated. Using the thermochemical cycle previously noted for the methylamines[5] the relative (relative to NH_4^+=0) heats of solvation in HSO_3F were obtained (Figure 2.2). $Me_3\overset{+}{P}H$ is only 5.7 Kcal/mole less favourably solvated than PH_4^+, whilst for the analagous amines $Me_3\overset{+}{N}H$ is 13.4 Kcal/mole less favourably solvated than NH_4^+. It has been argued that for the amine series the unfavourable effects of methyl substitution arise primarily from loss of

strong specific hydrogen bonds[5]. Beauchamp therefore suggests that hydrogen bonding to the conjugate acids of phosphorus is substantially weaker than for amines. This then accounts for the smooth increase in solution basicities observed for phosphines and the anomalous ordering observed for the amines.

Table 2.2

Relative heats of solvation in HSO_3F[c)]

Ion	$\delta_R\Delta H_s$[a,b)]
NH_4^+	0
$MeNH_3^+$	5.3
$Me_2NH_2^+$	8.9
PH_4^+	11.3
Me_3NH^+	13.4
Me_3PH^+	17.0

a) Reference 8 b) Kcal/mole c) Reference 4

Whilst the lower phosphines are moderate nucleophiles they are extremely weak acids and as expected the pKa's are decreased by aryl and increased by alkyl substitution (table 2.3)[10]. Removal of

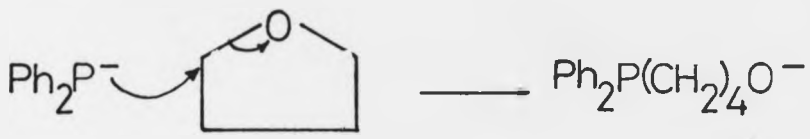
Table 2.3

pKa's of Phosphines

Ph_2PH	22	Et_2PH	34
$PhPH_2$	24	$t\text{-}Bu_2PH$	37
PH_3	29	PH_2^-	38-42
$C_6H_{11}PH_2$	32		

a proton requires powerfully basic conditions (e.g. Na/NH_3, BuLi or RMgBr) the resulting highly basic phosphide anions are very powerful nucleophiles and undergo a number of ususual reactions. For example diphenyl phosphide attacks the ether linkage of tetrahydrofuran

displacing alkoxide anion,[11]



and also attacks unactivated aromatic halogen compounds displacing fluoride[12], bromide or iodide ions[13]. The high nucleophilicity of phosphide anion results in very clean nucleophilic displacement reactions which are synthetically extremely useful.

Such reactions of alkali metal phosphides have been extensively investigated by Isslieb et al[14]. Metal Phosphides M_nPR_{3-n} are readily prepared by reductive or proton-transfer reactions (I-IV)

$$R_{3-n}PCl_n + 2nM \longrightarrow R_{3-n}PM_n + nMCl \quad [15] \qquad (I)$$

$$R_{3-n}PH_n + nBuLi \longrightarrow R_{3-n}PM_n + nBu - H \quad [16] \qquad (II)$$

$$R_{3-n}PH_n + nM \longrightarrow R_{3-n}PM_n + H_2 \quad [16] \qquad (III)$$

$$2RPH_2 + 2K \xrightarrow[RPH_2]{50\% \text{ excess}} 2RPHK + H_2 \quad [17] \qquad (IV)$$

(where M = Li, Na, K; R = Ph, alkyl, H; n = 1,2)

Reactions involving phosphorus hydrides (II-IV) give good yields with short reaction times and easy work up procedures. The hydride precursors may be prepared in good yield (~80%) by lithium-aluminium hydride reduction of the corresponding halides[18], and are useful stock reagents for generation of alkali-metal phosphides and in other synthetically useful procedures*. They have the disadvantage that they are expensive, not

* For example preparation of vinyl phosphines ref. 1(c)

readily available, and unpleasant to prepare on a large scale. Metal phosphides react rapidly with alkyl halides to afford good yields of alkyl phosphines (V-VII),

$$R_2PM + R'Cl \longrightarrow R_2PR' + MCl \qquad (V)$$

$$2R_2PM + Cl - (CH_2)_n - Cl \longrightarrow R_2P - (CH_2)_n - PR_2 \qquad (VI)$$

$$2RPHM + Cl - (CH_2)_n - Cl \longrightarrow \underset{H}{RP} - (CH_2)_n - \underset{H}{PR}$$

$$\downarrow BuLi$$

$$RR'P - (CH_2)_n PRR' \xleftarrow{2R'Cl} \underset{Li}{RP} - (CH_2)_n - \underset{Li}{PR} \qquad (VII)$$

$$n > 3$$

Reaction of a 1:1 molar ratio of diphenyl phosphide and a terminal dihaloalkane affords mainly polymeric and quaternised products and little of the synthetically useful chloro-alkyl phosphine (VIA)

$$R_2PM + Cl - (CH_2)_n - Cl \xrightarrow{\times} R_2P - (CH_2)_n - Cl \qquad (VIA)$$

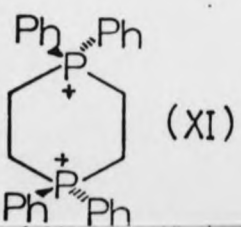
The reactions of phosphide anion or dianion with ethylene oxide[19] or oxetane[20] are useful giving the terminal alkoxides under mild conditions. This demonstrates the high nucleophilicity of phosphide anion since few nucleophiles will undergo this reaction e.g. sodium amide gives largely elimination under the same conditions.

$$Ph_2PLi + \text{(ethylene oxide)} \longrightarrow Ph_2P(CH_2CH_2OLi) \qquad (VIII)$$

$$\downarrow H_2O$$

$$Ph_2P(CH_2CH_2Cl) \quad (X) \xleftarrow{PCl_5} Ph_2P(CH_2CH_2OH) \qquad (IV)$$

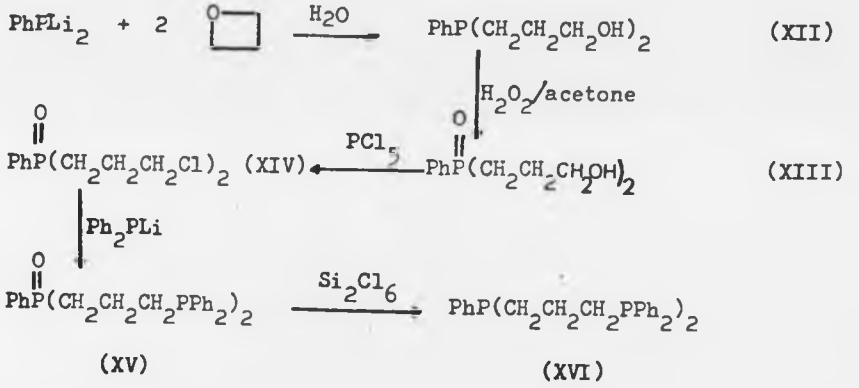
$$\searrow$$



(XI)

Attack of phosphide anion on ethylene oxide[19] is fast, there being no competitive reaction from the alkoxide (VIII) so produced. Hydrolysis of (VIII) affords the alcohol (IX) which may be halogenated (PCl_5) to give (X). Unfortunately halide (X) (a potentially useful intermediate to polyphosphines or cyclic systems) is unstable and rapidly quaternises at room temperature to give the salt (XI).

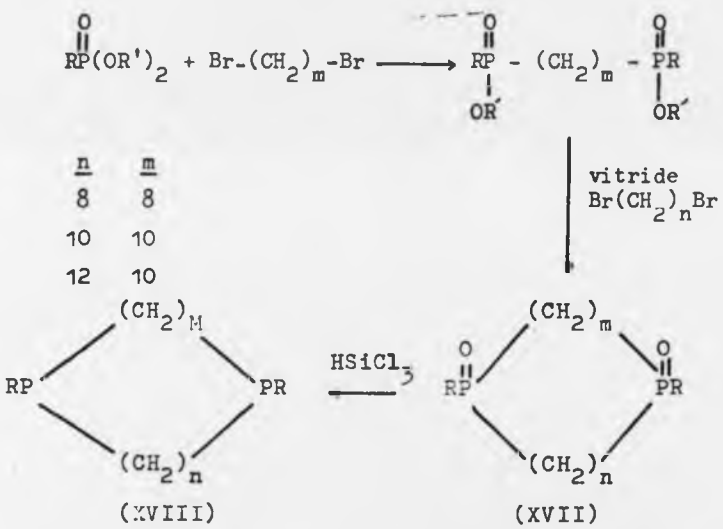
An analagous reaction[20] with oxetane has been used by Ibers et al to produce a tridentate phosphorus chelate (XVI), and demonstrates a useful method for overcoming the quaternisation problem.



Oxidation of the alcohol (XII) affords the oxide (XIII) which is blocked towards quarternisation and on halogenation gives the stable bis-halide (XIV). Sequential treatment of (XIV) with diphenyl phosphide and reduction with Si_2Cl_6 affords the desired ligand (XVI) in 55% overall yield.

B. The Michaelis-Arbuzov Reaction

The Michaelis-Arbuzov reaction of isopropyl phenyl phosphonite and alkyl bromides[21] affords alkyl phosphinates which in the presence of sodium bis(2-methoxyethoxy) aluminium hydride (vitride) and alkyl bromides yields linear phosphine oxides. T.H. Chan and B.S. Ong have used this reaction to prepare macrocyclic bis(phosphine oxides) (XVII) which on reduction with $HSiCl_3$ give macrocyclic diphosphines (XVIII) with retention of configuration*[3].



This route is clearly applicable to the synthesis of a wide variety of phosphorus containing macrocycles and since now proved, is an attractive synthesis of the mixed phosphorus/oxygen systems.

C. Criteria for Macrocycle Synthesis

J.M. Lehn has recently published a critical evaluation of the design criteria for macrocycle complexing agents[22]. This reviews

*Reduction of phosphine oxides by silanes is generally stereospecific[2], and with trichlorosilane has previously been reported to proceed with high retention of configuration[2].

this rapidly expanding field of research with particular reference to the macrocyclic ether or crown compounds and the macrocyclic nitrogen or cryptate compounds. Some of the most important points are briefly summarised:-

(a) High dilution conditions are generally required to depress the formation of oligomer or polymer.

(b) The cyclisation step should be as fast as possible to maintain very low stationary concentrations of reactants. The use of dipolar aprotic solvents such as tetrahydrofuran may be helpful in this respect.

(c) When flexible chains are co-condensed, they should be of comparable length.

(d) Introduction of hetero-atoms may remove or reduce steric barriers to cyclization.

(e) Cyclization yields may be dramatically increased by the 'template effect'. Alkali metal cations involved in cyclization reactions may themselves play this role.

(f) The introduction of rigid groups may increase the probability that the molecule is in a favourable conformation for cyclisation.

The metal phosphide/halide coupling reaction appeared to fit these criteria well. Accordingly the syntheses shown in figure (2.1) were envisaged, and attempted.

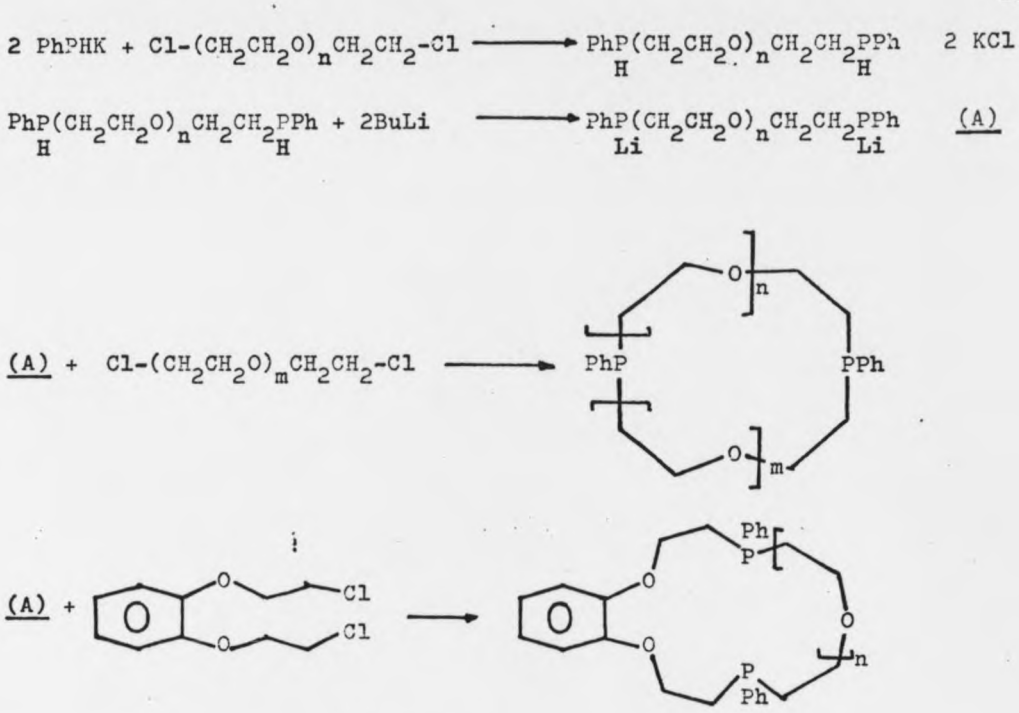

2 PhPHK + Cl-(CH2CH2O)nCH2CH2-Cl
PhP(CH2CH2O)nCH2CH2PPh
H H
2 KCl
PhP(CH2CH2O)nCH2CH2PPh + 2BuLi
Li Li
(A)
(A) + Cl-(CH2CH2O)mCH2CH2-Cl
PhP
PPh
(A) +
Cl
Cl
Ph
P
P
Ph

Figure 2.1.

Table 2.4

Linear Phosphino-ethers

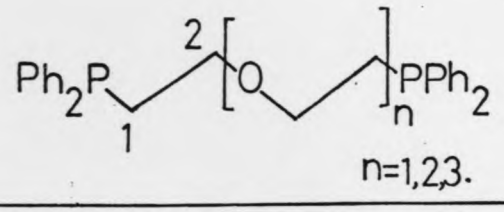
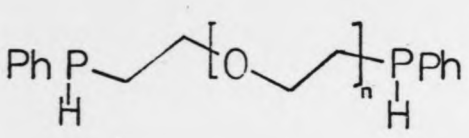
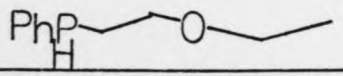
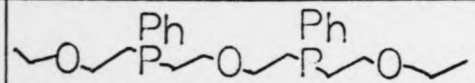
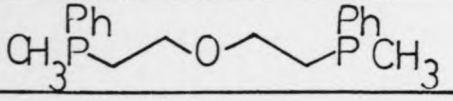
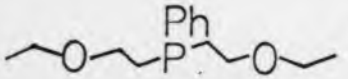
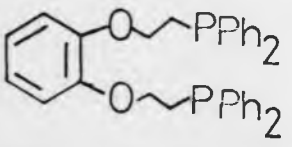
No.	Molecular formula		mw	B.p.(b)	% Yield(c)	Analysis
6 n=1	 n=1,2,3.	$C_{28}H_{28}O_1P_2$	442	180-190	71	Calc: C76.0, H6.3, P14.0 Found: C75.9, H6.1, P14.0
7 n=2		$C_{30}H_{32}O_2P_2$	486	190-210 mp 25-30	64	Calc: C74.1, H6.6, P12.8 Found: C74.1, H6.6, P12.4
8 n=3		$C_{32}H_{36}O_3P_2$	530	>220	61	Calc: C72.5, H6.8, P11.7 Found: C71.4, H7.1, P11.8
13 n=1		$C_{16}H_{20}O_1P_2$	290	170-180	72	Calc: C66.2, H6.9, P21.4 Found: C66.0, H6.8
14 n=2		$C_{18}H_{24}O_2P_2$	334	200-210	83	Calc: C64.7, H7.2, 09.6 Found: C64.5, H7.0, 08.8
15 n=3		$C_{20}H_{28}O_3P_2$	378	not distilled	68	Calc: C63.5, H7.4, P16.4 Found: C63.1, H7.2, P16.9
12		$C_{10}H_{15}O_1P_1$	182	70-85	76	Calc: C65.9, H8.24 Found C65.3, H8.04
27		$C_{24}H_{36}O_3P_2$	432	190-200	61	Calc: C66.4, 011.1, P14.3 Found: C66.1, 0.96, P14.3
28		$C_{18}H_{24}O_1P_2$	318	160-180	84	Characterised by spectra only.

Table 2.4 continued

No.	Molecular formula		mw	B.P.	% Yield	Analysis
-		$C_{14}H_{23}O_2P_7$	254	110-120	58	Characterised by spectra only.
23		$C_{34}H_{32}O_2P_2$	534	xst. solid decomp >120° air	61	Calc: C76.4, H6.0, 06.0, P11.6 Found: C77.0, H6.2

Notes (a) Quoted yields were those obtained after distillation. Yields may be increased by at least 10%, by hexane extraction of the crude reaction mixture, giving material of satisfactory purity for ligand complexation reactions.

(b) Short-path length molecular distillation under a diffusion pump vacuum. The quoted bp is the temperature of the oil bath at which distillation occurred. An ionisation guage was not available for monitoring the pressure accurately an error of ca ~ 10°C must be considered possible on these values.

(c) Products were typically very viscous oils. They were washed from the condensation probe with dry, degassed dichloromethane and were conveniently stored and used as standard solutions in dichloromethane.

Table 2.4 continued

SPECTRAL DATA

	^{1}H n.m.r.	I.r. (and mass spectra)
6	7.25(m, 20H, aromatic), 3.55(q, 4Hα to oxygen) 2.35(t, 4Hα to phosphorus), $J(H_1H_2)$ = 8.5 c/s	<u>Thin film</u>: the spectra of 6,7 and 8 were very similar apart from broadening and increased in intensity of the bonds at ca. 1100cm^{-1}, 3075(m), 3050(m), 2960(sh), 2910(sh), 2880(s), 1960(br,w), 1890(br,w), 1820(br,w), 1580(m), 1570(sh,w), 1480(s), 1440(s), 1360(s), 1310(w), 1250(w), 1210(w), 1190(vw), 1160(sh), 1130(sh), 1120(sh), 1100(s), 1070(s), 1030(m), 1005(m), 975(m), 920(sh), 900(w), 890(w), 855(vw), 750(sh), 740(vs), 700(sh), 695(vs).
7	7.25(m, 20H), 3.45 (m, 8H), 2.35 (t, 4H) $J(H_1H_2)$ = 8.5 c/s	
8	7.25(m, 20H), 3.45(m, 12H), 2.35(t, 4H) $J(H_1H_2)$ = 8.5 c/s	
13	7.25(m, 10H, aromatic), 3.35(d, 2H, J(P-H) = 60 c/s 3.35(m, 4H), 1.95(dt, 4H), $J(H_pH_1)$= 4.5 c/s $J(H_1H_2)$= 7.5 c/s	The thin film i.r. spectra of (13), (14) and (15), resemble the spectra of (6), (7) and (8), with the addition of a new band at 2290 cm^{-1} corresponding to ν(P-H). The mass spectrum of (13) showed strong peaks at m/e= 290*, 223, 207, 180, 160, 149, 136, 125, 108, 91, 78, 65, 58, 51, 43.
14	7.25(m, 10H), 4.2(bs, 2H), 3.5(m, 8H) 2.05(∂t, 4H), $J(H_pH_1)$ = 4.5 C/S, $J(H_1H_2)$ = 7.5 c/s	
15	7.25(m, 10H), 4.7(bs, 2H), 3.5(m, 12H) 2.0(dt, 4H), $J(H_1H_2)$ = 7.5 c/s	
12	7.25(m, 5H), 3.45(q + dq, 4H), 2.05(dt, 2H) 1.13(t, 3H), $J(H_pH)$ = 4.5, $J(H_1H_2)$ = 7.5, $J_{CH_3CH_2}$ = 7 c/s	The thin film i.r. spectra resembles that of (13). The mass spectrum showed strong peaks at m/e= 182*, 149, 136, 125, 121, 108, 91, 83, 78, 65, 51, 40, 32.
27	7.25(m, 10H), 3.45(m, 12H), 2.35(t, 8H), 1.13(t, 6H)	

* This peak is the molecular ion.

2.2 Results and Discussion

A. Linear Diphosphines

Terminal dichloroethers $Cl(CH_2CH_2O)_nCH_2CH_2Cl$ (n = 1-3:compounds numbered 1-3) were prepared by direct chlorination ($SOCl_2$, neat, >80°) from the corresponding glycols. The resulting oils were purified by aqueous work up, and subsequent careful* fractionation gave very faintly green liquids of characteristic odour, having a single g.l.c. peak.

Reaction of Ph_2PH (4) with BuLi in benzene/hexane (20°, 50:50 v/v) gave a lemon

$$Ph_2PH + BuLi \longrightarrow Ph_2PLi \qquad (5)$$

yellow precipitate of Ph_2PLi (5). Treatment of (5) with $Cl\text{-}(CH_2CH_2O)CH_2CH_2\text{-}Cl$ (1) caused the yellow colour of the solid to be discharged. Filtration, to remove LiCl, removal of

$$2Ph_2PLi + Cl\text{-}(CH_2CH_2O)CH_2CH_2\text{-}Cl \longrightarrow Ph_2PCH_2CH_2OCH_2CH_2PPh_2 + LiCl$$

benzene and hexane <u>in vacuo</u> and short path length molecular distillation afforded 1,5 <u>bis</u>(diphenylphosphino)-3-oxa pentane (6) as a faintly yellow viscous oil. Similarly obtained in good yield were $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (7 and 8) for n = 2 and 3, see table 2.4.

Reaction of excess $PhPH_2$(9) with potassium in boiling benzene gave PhPHK (10) as an orange/yellow solid, which on treatment with 1-chloro-3-oxa pentane (11) in benzene/hexane (50:50 v/v) gave a good yield of $PhPH\text{-}(CH_2CH_2O)Et$ (12) as a viscous yellow oil, which was subjected to short path length molecular distillation affording a colourless oil of distinctive odour. This reaction served as a model for the preparation of the <u>bis</u>-hydrido phosphines $PhPH(CH_2CH_2O)_nCH_2CH_2PHPh$ (13-15, n=1,2,3) which were accordingly prepared and purified by the same

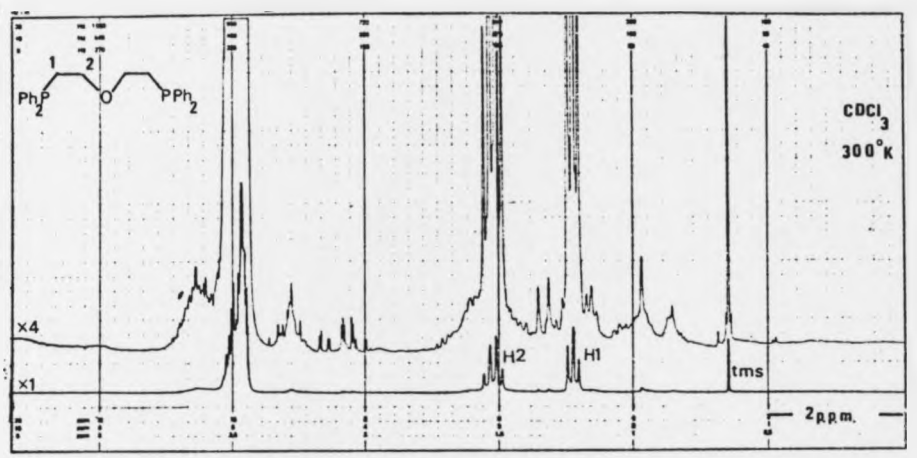
*Distillation required a Nester Faust Annular Spinning Bond unit.

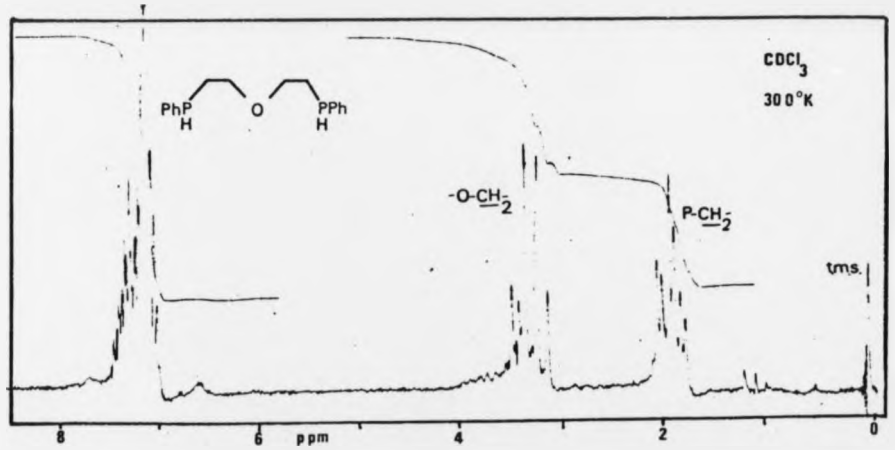
method from PhPHK and the dichlorides (1-3). The bis hydrido phosphines (13-15) were obtained as viscous slightly yellow oils and were further characterised by sequential reaction with BuLi and alkyl or ethoxy alkyl chlorides in benzene/hexane (50:50 v/v, 20°) to give the alkylated derivatives (27) and (28) in good yield, see table 2.4.

Representative ^1H n.m.r. and i.r. spectra for $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ and $PhPH-(CH_2CH_2O)_nCH_2CH_2PHPh$ (for n=1 and 2) are presented in figure 2.2. For example $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$ (7) gave good analytical figures and a moderately intense molecular ion in the mass spectrum. The i.r. spectrum shows a strong resemblance to that of other known linear alkyl phosphines with the addition of an intense C-O-C absorption at 1100 cm^{-1}. No bands corresponding to phosphine oxides were observed (νP=O, 1180, 1125 cm^{-1}). In the p.m.r. spectrum (C_6D_6), the methylene groups α and β to phosphorus appear as multiplets at 2.35 (t, 4H) and 3.54 (q, 4H) p.p.m. respectively and the methylene protons between the ether oxygens appear as a sharp singlet at 3.29 (s, 4H) p.p.m. The spectra of the mono-ether hydride (13), figure 2.2 were very similar to those of (7) with the addition of a P-H absorption in the i.r. at 2280 cm^{-1}. The p.m.r. (δ, $CDCl_3$) showed methylene signals at 1.95 (dt, 4H), 3.35 (m, 4H) and aromatic protons at 7.25 (m, 10H). The P-H signal appears as a widely spaced broad doublet (3.35 (d, 2H), J(PH) = 60 c/s). A moderately intense molecular ion was obtained in the mass spectrum and analytical results were reasonable.

The more rigid diphosphine, 2,2'-phenylene dioxy (bis) diphenylphosphino ethane (23) was prepared according to figure 2.3.

Figure 2.2. ^{1}H n.m.r. and I.r. spectra for some representative bis-phosphinoethers.





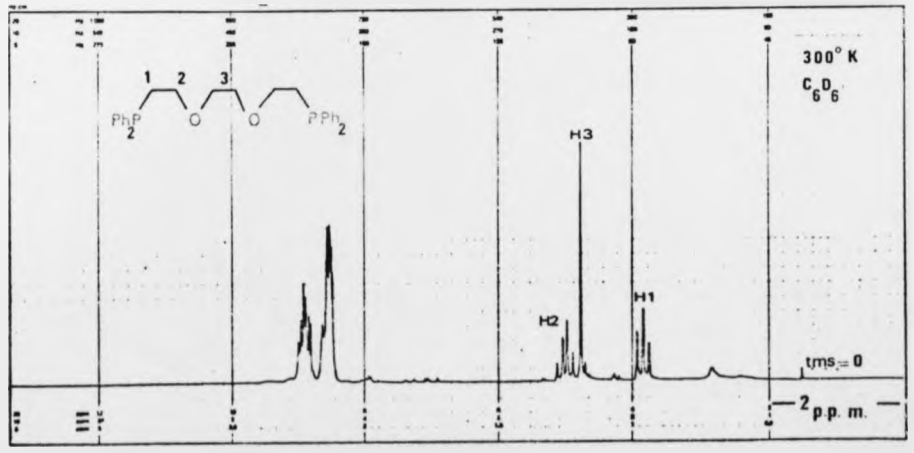
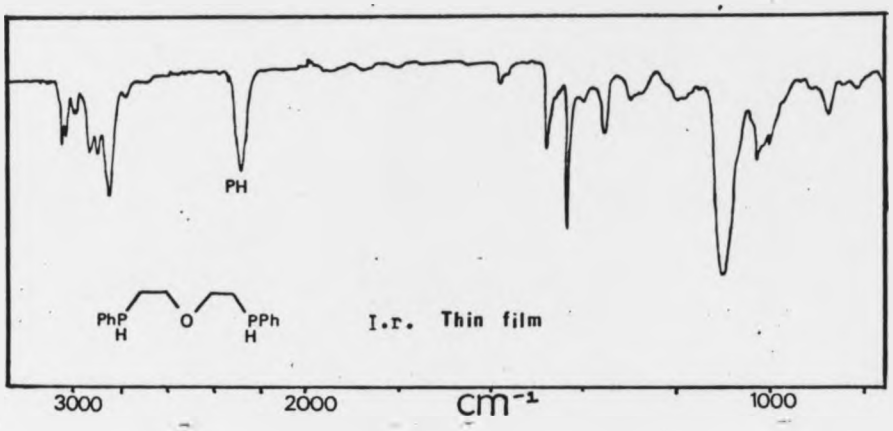


Figure 2.2. continued



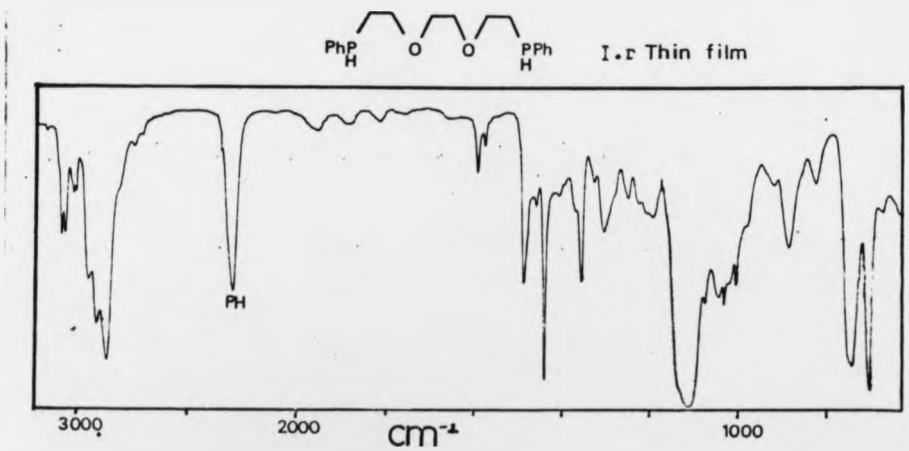
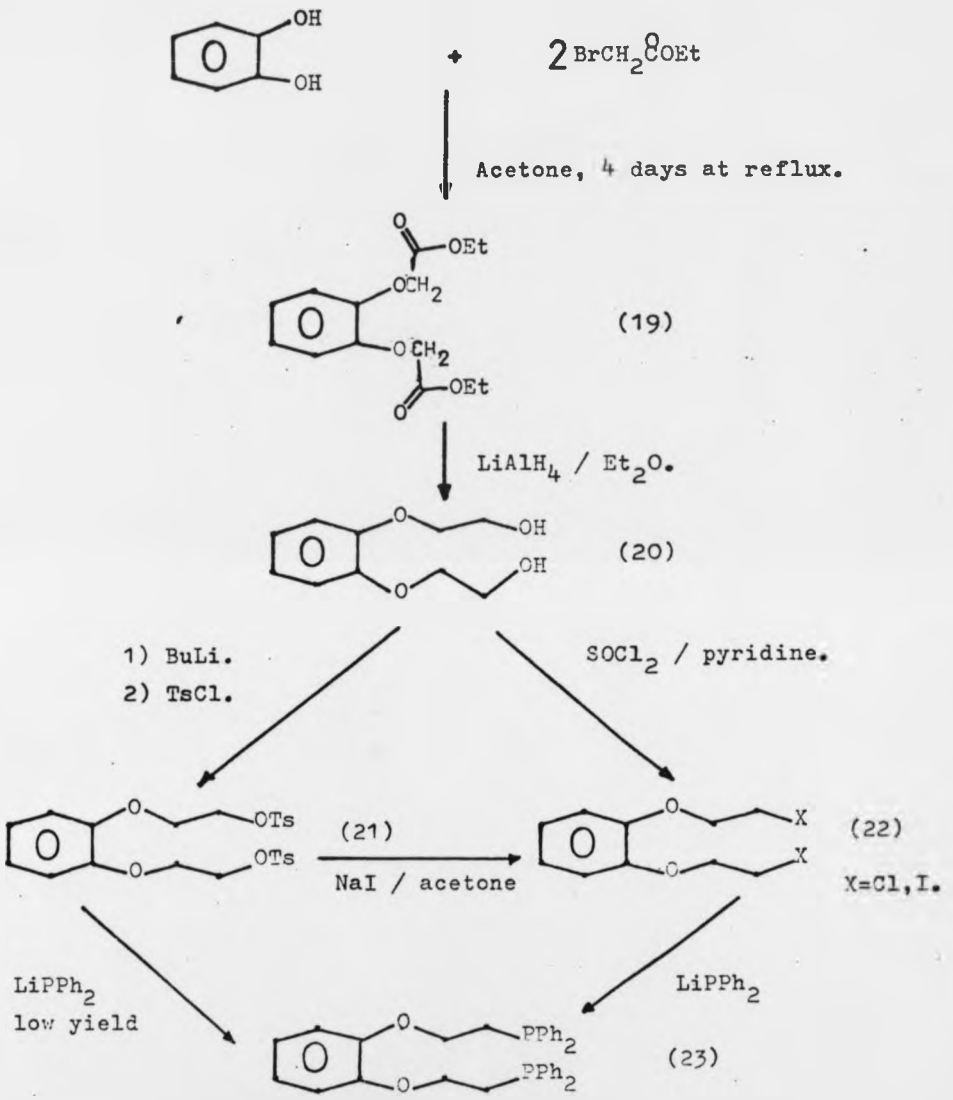


Figure 2.3. Synthesis of a more rigid phosphino-ether.



Condensation of catechol and ethyl bromoacetate in the presence of K_2CO_3 (reflux 4 days, acetone) gave, after aqueous work up and extraction with ether, diethyl phenylenedioxy (bis) acetate (19), as a viscous yellow oil which was not further purified. Reduction of this ester (19) ($LiAlH_4$, Et_2O at 0^o) gave 2,2´ - phenylenedioxy (bis) ethanol (20) in good yield as a crystalline white solid (rxst. CCl_4). Halogenation of the alcohol (20) using either $SOCl_2$/pyridine or by sequential reaction with BuLi, tosyl chloride and sodium iodide, gave 2,2´-phenylenedioxy (bis) chloroethane (22) as a crystalline white solid (rxst. CCl_4/hexane). Treatment of a suspension of $LiPPh_2$ (5) (benzene/hexane) with either the tosylate (21) or the chloride (22) gave 2,2´-phenylenedioxy (bis) diphenylphosphino ethane (23) in moderate yield as a white, air stable, crystalline solid (table 2.4).

B. Attempted Synthesis of Cyclic Diphosphines

The proposed cyclisation reaction shown in figure (2.4) were attempted under a variety of high dilution conditions without evidence of substantial success.

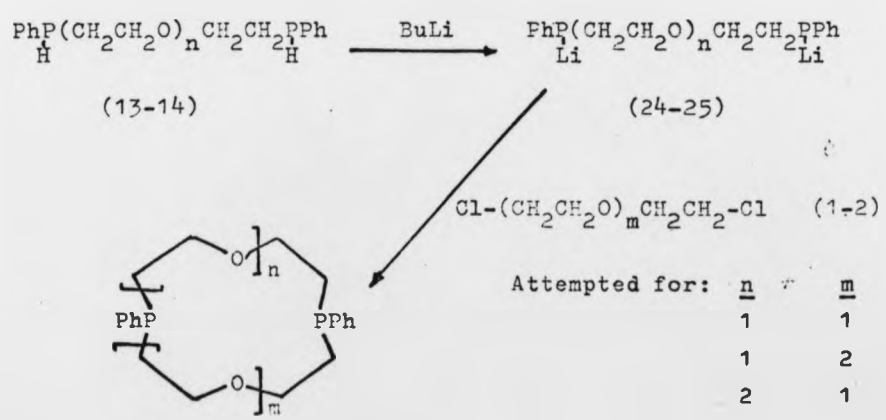


Figure 2.4.

Initial reactions were carried out heterogeneously this being dictated by the ease of preparation of suspensions of the appropriate dilithium phosphides. As previously noted, a fast coupling reaction implies low stationary concentrations of reactants during cyclization, to some extent mitigating the need for high dilution conditions. The reaction between phosphide and alkyl halide is certainly fast but attempts to quantify this by stopped flow kinetics were severely hampered by atmospheric oxidation of the phosphide. Reaction of a 10^{-3}M tetrahydrofuran solution of Ph_2PLi with a 100 fold excess of 1-chloro-3-oxa pentane (pseudo first order conditions) showed exponential loss of Ph_2PLi with $t_{\frac{1}{2}}<0.002$ secs (monitored by loss of the phosphide absorption at 460 n.m.). It could not be established that the observed reaction was not due to oxidation or both oxidation and the desired coupling reaction, a full kinetic study was therefore abandoned.

In the absence of quantitative evidence it was tentatively assumed that addition of a 10^{-3}M solution of the dihalides $Cl\text{-}(CH_2CH_2O)_nCH_2CH_2\text{-}Cl$ ((1) or (2), n = 1,2) to a refluxing suspension of the phosphides $PhP(CH_2CH_2O)_nCH_2CH_2PPh$ (24), (25), n = 1,2) might approximate to high dilution conditions.

<u>The Reaction of a Suspension of Di-lithium 1,5-bis(phenylphosphido)-3-oxa pentane (24) and 1,5-dichloro-3-oxa pentane</u>: 1,5-<u>bis</u>(phenylphosphino)-3-oxa pentane (13), (2g, 6.9mmole) in benzene/hexane (50 ml, 50:50, 20°C) was treated with BuLi (6.7 ml, of a 2.1 M solution in hexane, 14 mmole) affording a pale yellow precipitate of the diphosphide, solvent was removed by filtration and the solid was washed with benzene/hexane (2x 10 ml) and redispersed in the same solvent (100 ml). The refluxed and vigorously stirred yellow suspension was treated with 1,5-dichloro-3-oxa pentane (0.986g, 6.9mmole) in hexane (50 ml), dropwise over 2 hours.

The resulting almost colourless suspension of LiCl was treated with degassed Charcoal (norite) and filtered through celite. Removal of solvent in vacuo and subsequent heating in vacuo for 2 hours (50°, 10^{-3} mmHg) afforded a faintly yellow oil. The i.r. spectrum of this oil was very similar to that of the linear phosphino-ethers(6-8) but in addition showed a very weak impurity peak at 2281 cm^{-1} attributable to traces of P-H containing compounds. The ^{1}H n.m.r was also similar to that of (6-8) but the methylene resonances at 3.55 (m, 8H) and 2.35 (m, 8H) were broadened and showed little fine structure, and the proton integrals although usually within ~12% of the expected values, varied from run to run with no obvious trend. The mass spectrum showed no evidence of molecular ions corresponding to cyclic products and the general lack of any peaks in or above the region of 360 mass units (i.e. cyclic 1:1 addition product) implied highly polymeric material. The apparent absence of any low oligomeric species (linear or cyclic) was surprising, but since the molecular ions observed for the linear diphosphines (6-8) were weak, an unexpected* fragmentation pathway for this class of compound could not be ruled out.

A portion of the oil was subjected to short path-length molecular distillation. Apart from an unidentified volatile yellow oil (bp 70°, 10^{-4} mmHg) nothing distilled up to a temperature of c.a. 300° (10^{-4} mmHg) at which rapid decomposition occurred. Similarly attempts to fractionally crystallise a portion of the oil ($MeOH/Et_2O$ at $-80^{\circ}C$) resulted in no obvious purification and no crystalline products were obtained. In a repetition of this experiment the oil was oxidised to the corresponding phosphine oxides (excess aqueous H_2O_2 in acetone $<20^{\circ}$) affording a mixture of at least 8 highly hygroscopic products which were separated by thick layer chromatography (1 metre silica-gel plates, eluent Et_2O).

*linear diphosphines and particularly their oxides are reported to give very intense molecular ions as are the cyclic diphosphines reported in ref. 3.

The resulting yellow oils were subjected to mass spectrometry and F.T. ^{1}H n.m.r.. None of these products showed spectral characteristics consonant with cyclic material.

The reactions were repeated under high dilution conditions[xx]. The dilithium phosphides (24, 25) are very soluble in T.H.F. with which they react at a negligible rate at room temperature, and T.H.F. has frequently been found to give significantly improved yields (cf. ether or benzene) in crown-ether synthesis[22]. Accordingly 10^{-3} M T.H.F. solutions (20°) of dilithium phosphides (24 and 25) and dichloroethers (1 or 2) were slowly and concurrently* added to vigorously stirred T.H.F. Under these conditions the reaction of $PhPCH_2CH_2OCH_2CH_2PPh$ (Li, Li) with $Cl\text{-}(CH_2CH_2O)_2CH_2CH_2\text{-}Cl$ and subsequent aqueous work up, afforded a colourless oil. Similar results being obtained for the series of reactions represented in scheme (2.4). The ^{1}H n.m.r. and i.r. spectra were very similar to those obtained under inhomogeneous conditions, however the mass spectrum gave very tentative evidence, of a molecular ion corresponding to the 1:1 coupling product. Oxidation of the product to the corresponding phosphine oxides[20] (excess H_2O_2/acetone, <20°) gave a mixture of at least six products[+] which were separated by thick layer chromatography on silica gel (ether) and subjected to mass spectrometry and F.T. ^{1}H n.m.r.. None of these products showed spectral characteristics consonant with cyclic material.

*A peristaltic pump was used to ensure a constant and readily controlled addition rate for the reactants.

[+]These phosphine oxides (ν(P=O) = 1180(S), 1125(s)cm^{-1}) were very hygroscopic.

[xx]See Experimental.

Molecular models* indicated that any 15 membered cyclic phosphino-ethers present in the crude reaction mixture might be expected to readily complex with tetracarbonyl dirhodium dichloride by analogy with the proved reaction with linear phosphino-ethers (6-8) (hereinafter referred to as L_1, L_2 and L_3), figure 2.5.

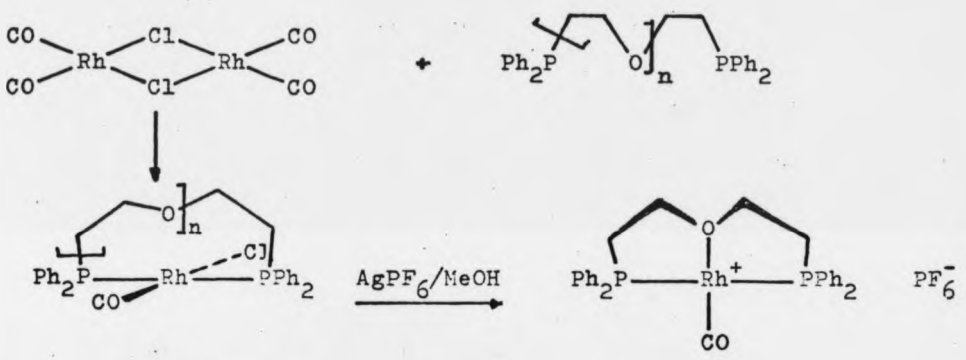


Figure 2.5. For n=1.

Accordingly sequential treatment+ with tetracarbonyl dirhodium dichloride and silver hexafluorophosphate gave amorphous beige/brown neutral and cationic complexes respectively (cf. $[RhL_nCO(S)]^+PF_6^-$, n = 1,2,3 which are bright yellow and highly crystalline from MeOH). These had i.r. and ^1H n.m.r spectra superficially similar to those of the known‡ linear

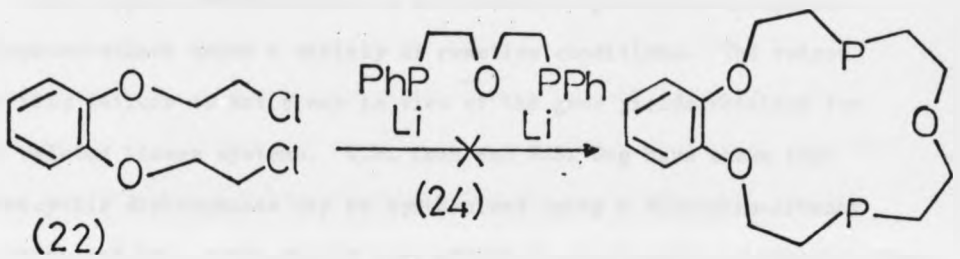
*cf. The crystal structures of $[RhL_nCO(S)]^+PF_6^-$ (where n = 1,2,3 and S = solvent) Chapter 3.

+Method identical to that used in the preparation of $[RhL_nCO(S)]^+PF_6^-$, Chapter 3.

‡This work Chapter 3.

phosphinoether complexes, but with very broadened absorptions. This indicated a mixture of compounds but no discrete cationic complexes could be isolated by recrystallization (MeOH) or chromatography (silica gel, diethyl ether).

A final alternative route was investigated using the more rigid dichloride (22).



(22) (24)

Concurrent slow addition of 10^{-3}M solutions of the dihalide (22) and dilithium diphosphide (24) to vigorously stirred T.H.F. (20°) and subsequent aqueous work up afforded a yellow oil which on pumping in vacuo for four days partially solidified giving a waxy solid. This was oxidised to the corresponding phosphine oxides (excess H_2O_2, acetone < 20°). which were hygroscopic (ν(OH), 3,400 (br)cm^{-1}) and had intense absorptions at 1185 and 1120 cm^{-1} (ν(P=O)). Mass spectrometry gave no evidence of cyclic material and the ^1H n.m.r. was not interpretable having an extended series of broad resonances in the range 3.5 - 1.5 p.p.m. (δ scale). It was concluded that predominantly polymeric products of unknown composition had been formed.

C. Conclusion

Linear phosphino-ethers and their hydrides may be readily prepared by the phosphide coupling reactions discussed. Using a phosphorus hydride as a starting reagent, sequential treatment with BuLi and an appropriate chloroether and subsequent work up may be conveniently

carried out in a single reaction vessel, facilitating the rapid handling of the air sensitive materials involved. The ligands so produced are in general sufficiently pure (after hexane extraction) to use directly in complexation reactions. They are obtained as viscous slightly yellow oils, having very characteristic i.r. and n.m.r. spectra and are most conveniently handled and stored as standard CH_2Cl_2 or benzene solutions.

This type of reaction has so far failed to produce macrocyclic phosphino-ethers under a variety of reaction conditions. The reason for this failure is not clear in view of the good yields obtained for the related linear systems. T.H. Chan and B.S. Ong have shown that macrocyclic diphosphines may be synthesised using a Michaelis-Arbuzov reaction and this route should also afford the macrocyclic phosphino-ethers.

2.3 Experimental Technique and Results

The techniques, instrumentation and reagents described are generally applicable except where specifically noted in text. All alkyl and aryl phosphines and organometallic complexes (Chapter 3) were handled under an inert nitrogen atmosphere except where it was either known or definitely established that this was unnecessary.

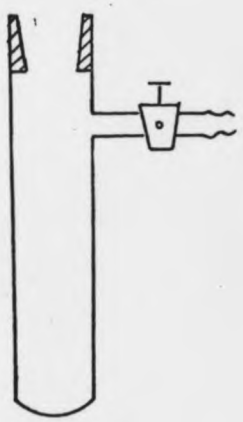
Handling of Air or Moisture Sensitive Materials

Modified Schlenck techniques were used[25]. All operations were carried out in apparatus which had been evacuated and filled with nitrogen, and subsequent operations were under a pressure of nitrogen (2 cms Hg) from a pressure equalised line. Schlenck tubes volumes of (2 - 800 ml) with 'Rotoflow' greaseless teflon vacuum taps were used extensively for the preparation and storage of air sensitive materials (Fig. 2.6). A vacuum manifold having two three-way taps supplying either a vacuum or nitrogen via pressure tubing facilitates the evacuation/N_2 flushing procedure. Figure 2.7 shows the vacuum manifold used for filtration on a semi-micro scale and the technique employed is easily modified to cope with extraction, separation or recrystallization in the 20 mg to 100 g scale. Rubber septa may be used to seal Schlenck tubes and this allows easy addition or removal of liquids by syringe. With care very sensitive materials are readily handled with several advantages over all glass vacuum line methods:

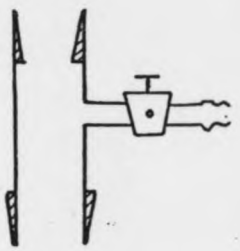
(a) The need for complex and reaction specific all glass apparatus with the attendant difficulties of cleaning, greasing and clamping such arrangements is avoided. Any reaction vessel fitted with a simple adaptor becomes an effective Schlenck tube.

(b) The use of teflon taps and rubber septa prevents contamination with vacuum grease.

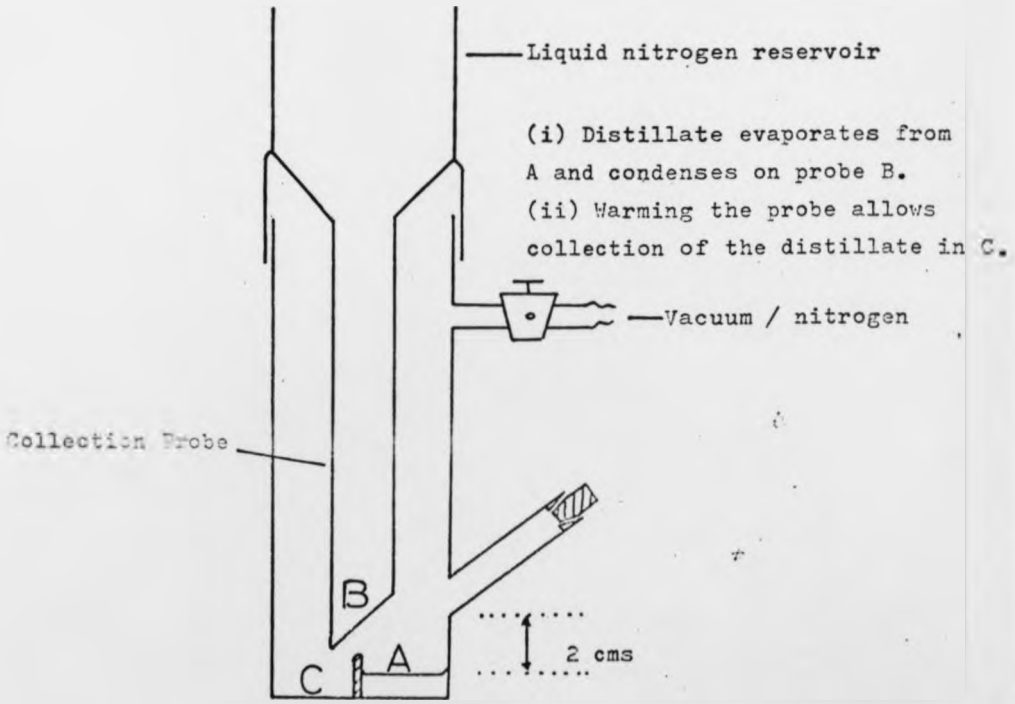
Figure 2.6



Schlenck Tube



Schlenck Adapter



Molecular Distillation Unit

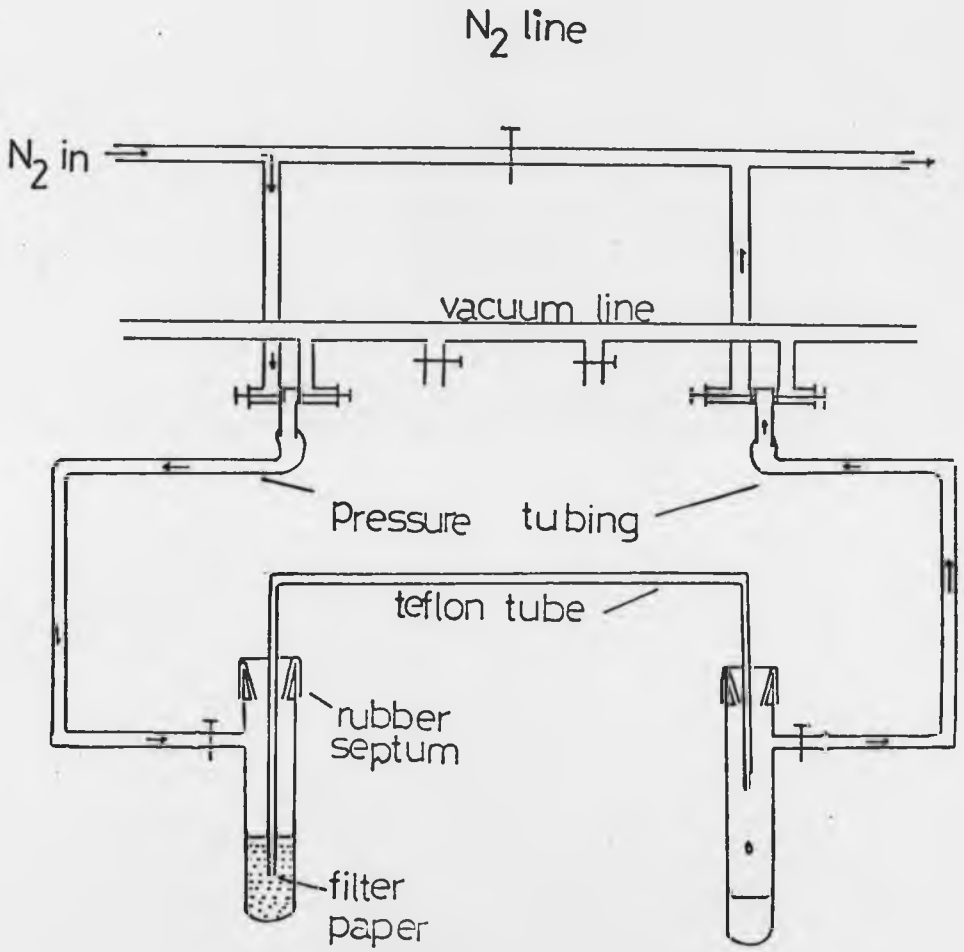

N_2 line
N_2 in
vacuum line
Pressure tubing
teflon tube
rubber septum
filter paper

FIGURE 2.7.

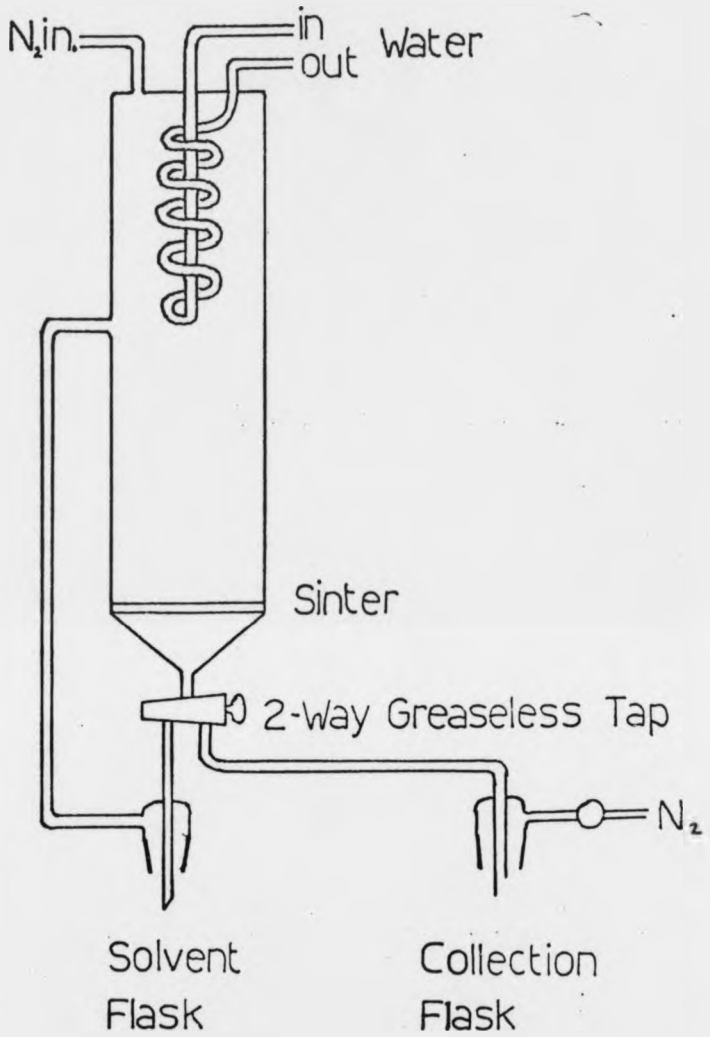

N_2 in.
in
out
Water
Sinter
2-Way Greaseless Tap
N_2
Solvent Flask
Collection Flask

FIGURE 28

A nitrogen filled dry box equipped with entry port was used for the preparation of mulls for spectroscopy, storage of sensitive reagents and similar operations. Both the entry port and box were continuously purged with dry nitrogen. Open dishes of phosphorus pentoxide and sodium hydroxide pellets were used to remove traces of water and acid or basic fumes.

Distillation Apparatus

Bulk solvents were distilled off suitable drying agents using a specially designed still (fig. 2.8) suitable for distillation, nitrogen out-gassing, storage and delivery of solvents under inert atmosphere.

Routine distillations (5-500 ml) were carried out using vacuum jacketed Vigreux columns with integral Perkin Triangles. More difficult separations were carried out using a 'Nester-Faust' annular teflon, spinning band, distillation unit. Low to medium boiling liquids (maximum bp ca. $180^{\circ}/10^{-4}$ mm Hg) were distilled using jacketed semi-micro stills. Very high boiling liquids, which include most of the linear phosphinoethers described in this chapter, were subjected to short path length molecular distillation. This is a non-equilibrium technique[26], requiring the distance between the points of evaporation and condensation to be less than the mean free path of the evaporating molecules at the pressure in question. Accordingly an apparatus having a pathlength of less than 1.5 cms was used at pressures of around 10^{-4} mm Hg (fig 2.9)

Instrumentation

Routine ^{1}H nmr. spectra were recorded using a Perkin Elmer R12 spectrometer. ^{1}H, ^{13}C, ^{31}P and variable temperature spectra were recorded on a Bruker WH90 pulse fourier transform spectrometer. All chemical shifts are quoted in p.p.m. on the δ scale.

Infra-Red spectra were recorded on Perkin Elmer 257, 457 and 621

instruments, as solutions or mulls. Far infra-red spectra were recorded on a R.I.I.C. FS-720 fourier transform machine and the resulting spectra were computed and plotted using a program rewritten by Dr. N.W. Alcock. Samples were run under vacuum as very thick nujol mulls between polystyrene plates.

U.v. spectra were recorded on Unicam SP800 and SP500 or Cary 14 spectrophotometers. Mass spectra were recorded on a Micromass 12 spectrometer and reference spectra were calibrated using perfluoro-kerosene as standards.

Melting points of non-sensitive materials were recorded on a Reichert/ Shandon hot stage microscope and sensitive materials were measured in sealed capillary's.

Chemicals and Reagents

All purchased reagents and chemicals were high grade materials from normal sources unless otherwise stated. Aryl-chloro phosphines were given by Maybridge Chemicals Ltd who also made facilities available for small scale 'plant' preparations of phenyl and diphenyl phosphines.

Nitrogen on line in the laboratory was B.O.C. 'white spot' grade and was further purified by passage through conc. sulphuric acid, sodium hydroxide and finally a 4 ft column of 'Lindt' 4A molecular sieve.

Solvents

Spectrograde and spectrosol spectroscopic solvents were supplied by Fisons and Hopkins and Williams Ltd respectively. Deuterated solvents were obtained from Prochem Ltd.

Commercial A.R. solvents were further purified for organometallic work as follows, and were stored in 1 litre Schlenck bottles under nitrogen.

Toluene, benzene, diethyl-ether and tetrahydrofuran were distilled off lithium aluminium hydride and stored over sodium wire.

Hexane, pentane and other alkanes were stirred over concentrated sulphuric acid, washed with water, dried over anhydrous potassium carbonate and distilled off lithium aluminium hydride.

Dichloromethane, chloroform and carbon tetrachloride were distilled off phosphorus pentoxide and stored over anhydrous sodium sulphate.

Methanol and ethanol were doubly distilled off magnesium turnings and stored over molecular sieve (Linde 3A).

Acetone was distilled off potassium permanganate, washed with aqueous sodium bicarbonate, dried, distilled and stored over anhydrous sodium sulphate, being further dried immediately prior to use by passage through a short column of anhydrous silica gel.

High Dilution Reactions:

In the synthesis of the polyoxa macrobicyclic diamines or cryptates a typical procedure is the condensation of a diamine and a diacidchloride under high dilution conditions. This involves slow addition of dilute solutions (circa 0.1 M) of the reagents to very rapidly stirred solvent (stirring speeds of up to 10,000 rev./min. are not uncommon).Low yields have been reported if mixing is inefficient and it has been suggested that rapid stoichiometric mixing of the reagents is probably the most important consideration in reactions of this type.[27] In contrast many of the syntheses of the crown ethers, involving condensation of diols (or ditosylates) with dichlorides give high yields with no stringent requirement for high speed stirring. This may reflect a much faster reaction for the diamine/diacidchloride system compared to that of the diol/dichloride system.Since the coupling reaction between a phosphide

and a chloride is thought to be very fast it was decided that high dilution technique should be used as far as possible. This is complicated by the extreme air sensitivity of the phosphide reagents used. The following experimental procedure is typical of that adopted in this work:

The reaction of 10^{-2} M T.H.F. solutions of dilithium-1,5-bis(phenylphosphido)--3-oxa pentane (24) and 1,5-dichloro-3-oxa pentane (1)

A 10^{-2} M solution of 1,5-dichloro-3-oxa pentane (0.429g, 3 mmole) in degassed T.H.F. (300ml) was prepared and stored under nitrogen in a septum sealed Schlenck flask. Similarly a 10^{-2} M solution of the dilithium phosphide (24) was prepared by treating 1,5-bis(phenylphosphino)--3-oxa pentane (13),(0.87g, 3 mmole) in T.H.F. (300ml) with BuLi (2.86ml, 6 mmole of a 2.1 M hexane solution) to give a bright orange/yellow solution. The two reagent flasks were linked to a central reaction flask (1l) by two lengths of small bore teflon tubing passing through the septum seals. The reaction flask contained 100ml of degassed T.H.F. which was magetically stirred at circa 800 to 1,000 rev./min. . Using a peristaltic pump the reagents ((1) and (24)) were added dropwise at circa 1 ml/min. to the reaction flask. To promote better mixing and dilution of the reagents one of the two inlet tubes was led beneath the surface of the T.H.F. . During the addition the reaction mixture became slightly turbid and faintly yellow, but no bulk precipitate of LiCl was observed. When addition was complete the reaction mixture was stirred for a further 30 minutes. Solvent was removed in vacuo and 100ml each of ether and water were added to dissolve the resulting sticky residue. The organic layer was separated

* See text

and the aqueous layer was extracted twice more with ether (2x50 ml). The ether extracts were combined and dried with anhydrous sodium sulphate . Solvent was removed *in vacuo* and volatile impurities were removed by pumping *in vacuo* (80^{o}, 10^{-3}mmHg) for a further three hours. There was thus obtained 0.8g of a very viscous yellow oil.

^{1}H n.m.r. ($CDCl_3$): 7.3(broad, 10H, aromatic), 3.7(broad, singlet, ~8H), 2.4(broad singlet, ~8H).

I.r. (nujol): This closely resembles that reported for compounds (6),(7) and (8), see table 2.4 . However this spectrum lacked the sharpness of the latter spectra.

Mass spectrum: A *very* weak molecular ion may have been observed at m/e = 360. The second heaviest peaks observed had m/e = 288 and 289. This may correspond to ions of the type $(PhPCH_2CH_2OCH_2CH_2PPh)^{+}$. The remaining principle peaks were found at m/e = 273, 261, 217, 186, 152, 136, 124, 108, 91, 78, 62, 51, 39, 28.

Oxidation of the above cyclisation products to the phosphine oxides

The oil obtained from the above preparation (0.4g) was dissolved in acetone (10ml) and cooled on ice. A solution of hydrogen peroxide (1ml of 30% aqueous H_2O_2 in 2ml of acetone, *circa* 10 fold excess) was added slowly with stirring so that the temperature did not rise above 20^{o}. Solvent was removed *in vacuo* and the remaining oily residue was heated at 80^{o}(10^{-3}mmHg) for 5 hours to remove volatile impurities. there was thus obtained 0.4g of a very viscous yellow oil, which was very hygroscopic. I.r. of the crude product showed $\nu(P{=}O)$ = 1180 cm^{-1}. The product mixture was chromatographed by thick layer chromatography on metre silica gel plates, with ether as eluent. Six prominent bands were observed and the products were extracted from the silica gel with dichloromethane, and were finally obtained as very viscous

faintly yellow oils in circa 20 to 40mg quantities. These products had very broad fourier transform ^{1}H n.m.r. spectra (peaks at about 7.3 and 2-4 p.p.m.) and could not be identified.

The above cyclisation reaction was repeated with different initial concentrations of reactants (10^{-1}M and 10^{-3}M) with no substantial evidence of successful cyclisation. Using concentrations as low as 10^{-3}M considerable atmospheric oxidation of the phosphide reagent occured. Similarly attempts to use mechanical high speed stirrers (Anderman multispeed) resulted in atmospheric oxidation of the reactants. The reaction was also repeated under inhomogeneous conditions as described in text.

1-chloro-3-oxa pentane (11)

Thionyl chloride (64 ml, 0.55 m, 10% excess) was added dropwise to β-ethoxy ethanol (45 g, 0.5 m) at 45°-50°. The mixture was refluxed for two hours and excess thionyl chloride was removed in vacuo . Pentane was added (100ml) and the mixture was washed with aqueous sodium hydroxide and dried over anhydrous sodium sulphate. Fractional distillation of the resulting black oil gave 1-chloro-3-oxa pentane (11), 32.5g, 60%, as a colourless mobile liquid, boiling at 108° at 76 cmHg. ^{1}H n.m.r. (CCl_4): 1.16(t, 3H), 3.55(q+t, 6H). Similarly prepared from the corresponding glycols were 1,5-dichloro-3-oxa pentane (1), 1,8-dichloro-3,6-dioxa octane (2), and 1,11-dichloro-3,6,9-trioxa undecane (3) . Commercially available glycols (R. Emmanuel Ltd.)

are contaminated (>20%) with higher and lower polyethylene glycols. Spinning band distillation of the resulting mixtures of halides was necessary to effect good separation, the purity being checked by g.l.c. (2ft SE30 silicon rubber column, isothermal 190-195°, He at 40 ml/min).

1,5-dichloro-3-oxa pentane (1)

Yield 80%, colourless liquid, bp 75°/20 mm Hg.

1,8-dichloro-3,6-dioxa octane (2)

Yield 71%, colourless liquid, bp 122°/16 mm Hg.

1,11-dichloro-3,6,9-trioxa undecane (3)

Yield 60%, faintly green liquid, bp 157°/16 mm Hg.

Diphenyl Phosphine (4)[18]

To $LiAlH_4$ (21g, 0.55 m, 10% excess) in diethyl ether (15 l) at -20° was added Ph_2PCl (220.5g, 1.0 m) in ether (3 l) dropwise, with vigorous stirring over 3 hours. The mixture was stirred for a further hour at room temperature. Wet ether (1 l) was very cautiously added, with cooling, followed by saturated aqueous NH_4Cl (10 l). The mixture was stirred until all the salts had dissolved, the organic phase was separated and extracted with ether (3 x 500 ml), and the combined organic extracts were dried over anhydrous Na_2SO_4. Fractionation in vacuo (138°/10 mm Hg) gave Diphenyl Phosphine 121g, 65% as a colourless, evil smelling, spontaneously inflammable liquid. For $C_{12}H_{11}P_1$ mw 186: Calc. C, 77.4 H, 5.9; P, 16.7 Found: C, 77.1, H, 6.0. ^1H nmr. ($CDCl_3$): ~7.9 (br, m, 12H), 4.57 (d, J(P-H) = 261 c/s, 1H). I.r. (Thin film): ν(P-H) 2280 (m,br).

Phenyl Phosphine (9)

was prepared above as a colourless, spontaneously inflammable liquid. Yield 60%, bp 40°/10 mm Hg.

^{1}H nmr. ($CDCl_3$): ~7.85 (br, m, 5H), 4.66 (d, J(P-H) = 260 c/s, 2H)

i.r.(Thin Film): ν(P-H) 2280 (m, br).

Lithium Diphenyl Phosphide (5)

was prepared by a slightly modified method of Isslieb[14]. Diphenyl phosphine (5g, 0.0269 m) in hexane (200 ml) at 20° was treated with BuLi (12.8 ml, of a 2.1 M solution in hexane, 0.269 m) with stirring, affording a bright yellow suspension of lithium diphenyl phosphide in virtually quantitative yield. In subsequent reactions it was found convenient to prepare and use this reagent in situ without further purification.

Potassium Phenyl Phosphide (10)

was prepared by the method of Isslieb[14] by refluxing potassium metal with phenyl phosphine in benzene (1:2 molar ratio) until a uniformly bright yellow suspension of potassium phenyl phosphide was obtained (ca. 24 hours). Benzene and excess phenyl phosphine were removed by filtration and the yellow solid was washed with benzene and dried in vacuo. The resulting highly air sensitive yellow solid was sealed in glass ampoules under vacuum (ca. 2 g qualities). A sample thus treated has shown no signs of decomposition after 9 months.

1,5-bis(diphenylphosphino)-3-oxa pentane (6)

A yellow suspension of lithium diphenyl phosphide (0.0269 m) in hexane (200 ml) was prepared as previously described. 1,5-dichloro-3-oxa pentane (1.925g, 0.0135m) in hexane (20 ml) was added dropwise to the stirred

suspension (20°), an exothermic reaction occurs and the yellow colour of the solid disappears. Lithium chloride was allowed to settle and the supernatant liquid was filtered through celite. Hexane was removed in vacuo and the resulting viscous yellow oil was subjected to short-path molecular distillation at 180-190°/10^{-4} mm Hg. There was thus obtained: 1,5-bis(diphenylphosphino)-3-oxa pentane (6) 4.3 g, 71% as a faintly yellow air sensitive oil. Analaytical and spectroscopic data are tabulated in the text.

Similarly was obtained: 1,8-bis(diphenylphosphino-3,6-dioxa octane (7) and 1,11 bis(diphenylphosphino)-3,6,9-trioxa undecane (8).

1,5-bis(phenylphosphino)-3-oxa pentane (13)

1,5-dichloro-3-oxa pentane (0.506g, 3.5 mmole) in hexane (10 ml) was added dropwise to a stirred suspension of potassium phenyl phosphide (1.048g, 7.0 mmole) in benzene/hexane (20 ml, 50:50) at 20°, causing the yellow colour of the phosphide to disappear. The resulting white suspension was treated as above, affording a very viscous colourless oil which was subjected to short-path molecular distillation (170-180°/10^{-4} mm Hg). There was thus obtained: 1,5-bis(phenylphosphino)-3-oxa pentane (13), 0.7 g , 72%, as a colourless spontaneously inflammable viscous oil. Analytical and spectroscopic data are tabulated in the text. Similarly was obtained 1,8 bis(phenylphosphino)-3,6-dioxa octane (14) and 1,11-bis(phenylphosphino)-3,6,9-trioxa undecane (15).

1,5-bis(phenyl-ethoxyethyl-phosphino)-3-oxa pentane (27)

1,5-bis(phenylphosphino)-3-oxa pentane (0.5g, 1.7 mmole) in benzene/hexane (50 ml, 50:50) was treated with BuLi (1.64 ml of a 2.1 M solution in hexane, 3.4 mmole) affording a very pale lemon yellow precipitate of

the diphosphide. Solvent was removed by filtration and the solid was washed with benzene/hexane (2 x 10 ml) and redispersed in the same solvent (50 ml). 1-chloro-3-oxa pentane (1) (0.372g, 3.4 mmole) in hexane (10 ml) was added in the cold, dropwise over 10 mins. The resulting colourless suspension of LiCl was allowed to settle overnight and the supernatant liquid was filtered through celite. Solvent was removed *in vacuo* affording a viscous yellow oil which was subjected to short-path molecular distillation. There was thus obtained 1,5-*bis*(phenyl-ethoxyethyl-phosphino)-3-oxa pentane 0.46g, 61% as a viscous oxygen sensitive, colourless oil. Analytical and spectral data is tabulated in text.

Diethyl phenylenedioxy(*bis*) acetate (19)

Catechol was twice recrystallised from CCl_4/EtOH. Catechol (23.5g, 0.213 m), ethylbromoacetate (71g, 0.426 m) and potassium carbonate (~59g, ~0.426 m) were refluxed in acetone for 4 days. Acetone was removed *in vacuo* and water (500 ml) was added. The mixture was extracted with ether (4 x 100 ml) and the combined extracts dried with anhydrous sodium sulphate. Solvent was removed *in vacuo* and the resulting pale brown viscous oil was heated *in vacuo* (70°/1 mm Hg, 3 hours) to remove traces of unreacted ethylbromoacetate. There was thus obtained Diethyl phenylenedioxy(bis)acetate .44g, 73.5% as a brown oil which was used without further purification. ^{1}H nmr. (CCl_4):
1.19(t,6H), 4.1(q,4H), 4.6(s,4H), 6.82(s,4H).
i.r. (thin film): 3000 (br,s,C-H), 1760(br,s), 1600(m), 1500(s), 1450(br,m), 1380(m), 1180-1280(v.br, v.s), 1140(m), 1120(m), 1070(m), 1030(m), 930(br,w), 860(w), 755(m , aromatic).

2,2'-phenylenedioxy-(bis) ethanol (20)

The ester (19) from above (44g, 0.156 m) in ether (250 ml) was added dropwise to a cooled stirred suspension of $LiAlH_4$ (13.0g,0.312m + 10%) in ether (500 ml). On completion of addition the mixture was refluxed for 30 minutes and cautiously decomposed with aqueous HCl (10%, 300 ml). The organic layer was separated and the aqueous layer was repeatedly extracted with boiling CH_2Cl_2 (6 x 150 ml). The combined organic extracts were dried over anhydrous sodium sulphate and solvent removed in vacuo to afford an off-white solid. Recrystallization from boiling CCl_4 gave 2,2'-phenylenedioxy(bis)ethanol, 23g, 75%, as fine white needles (mp 83°). ^{1}H n.m.r.($CDCl_3$): 3.95(M,8H), 4.1(s,2H(OH)), 6.85 (s,4H).

i.r. (Nujol): 3500(m, ν(O-H)), 1600(m), 1500(s), 1340(m),1295(m), 1260(s), 1220(s), 1130(s), 1080(s), 1045(s), 915(m,br), 745(m,br,aromatic).

2,2'-phenylenedioxy(bis)Chloroethane (22)

Attempts to chlorinate the diol (20) from above using phosphorous halides,oxalyl chloride or neat thionyl chloride under a variety of conditions failed to give good yields of the desired dichloride. For small scale runs a good yield was obtained using $SOCl_2$/pyridine/$CHCl_3$, but this reaction gave a very poor yield on scaling up the quantities and the reason for this behaviour was not established.

To the diol (20) (1g,5.05 mmole) in $CHCl_3$ (10 ml) was added pyridine (1.106g, 14mmole) To the stirred and refluxed solution was added thionyl chloride (1.31g,11 mmole) in $CHCl_3$ (10 ml) dropwise over 10 minutes. The resulting solution was stirred at 20° overnight. An additional 10 ml of $CHCl_3$ was added and the mixture was extracted with 10% HCl (3 x 5 ml), washed with sodium bicarbonate solution (2 x 5 ml) and dried over potassium carbonate. Solvent was removed in vacuo to give a

pale yellow oil. Recrystallization from CCl_4/hexane gave 2,2'-phenylene dioxy(bis)chloroethane 0.82g, 70%, as slightly off white needles (mp 52.5-53)

^1H nmr. ($CDCl_3$): 3.75(t,4H,JH_1H_2 = 8.5 c/s)
4.2(t,4H,JH_1H_2 = 8.5 c/s)
6.9(s,4H)

i.r. (Nujol Mull): 1600(m), 1505(s), 1420(m)
1330(m), 1300(s), 1260(s)
1220(vs), 1200(sh,s), 1125(s), 1080(m), 1035(s)
980(m), 920(m), 890(m), 750(vs).

Ditosylate of 2,2'-phenylenedioxy(bis)ethanol (21)

To a stirred suspension of sodium hydride (0.243g,10.1mmole) in ether (25 ml) was added the diol (20) (1g,5.05mmole) in ether (20 ml) at 20°. The mixture was refluxed until evolution of hydrogen had ceased (approx. 2 hours) affording a white suspension of the bis alkoxide. Tosyl chloride (1.925g, 10.1mmole) in ether (20 ml) was added dropwise and the mixture refluxed for a further hour. Water was added (100 ml) and the ether layer separated. The aqueous phase was extracted with ether (3 x 10 ml) and the combined ether extracts were dried over anhydrous sodium sulphate. Solvent was removed in vacuo giving a pasty crystalline solid, shown by n.m.r. to contain unreacted diol (20) (a trace) and tosyl chloride (~1%). Recrystallization from boiling ether/ethanol gave the Ditosylate, 2.0g, 80%, as white needles (mp 97°)
t.l.c. on fluorescent silica gel gave one spot R.F. 0.32 (eluted with ether)

^1H n.m.r. ($CDCl_3$): 2.4(s,6H), 4.2(m,8H)
6.8(s, 4H), 2.73 (d, 2 x 2H, JHH' = 8.5c/s), 2.23(d, 2 x 2H, JHH' = 8.5c/s)
i.r. (Nujol mull): 1600(s), 1505(s), 1400(w,sh)
1360(m), 1100-1300 (v. complex strong multiplets), 930(s,br)
820(s), 790(s), 755(s), 670(s).

2,2'-phenylenedioxy(bis)iodoethane (22)

To the ditosylate (21) (0.1g, 0.20 mmole) in acetone d^6 (1 ml) was added anhydrous sodium iodide (0.0594g, 0.40 mmole). The reaction was monitored by n.m.r. and conversion to the di-iodide was complete in 3 hours. Recrystallization from 60-80° petrol-ether gave 2,2'-phenylenedioxy(bis)iodoethane (22) 0.09g as a white crystalline solid, mp 72-74°.

^1H n.m.r. (Acetone d^6) : 3.55(t, 4H, JHH' = 6c/s), 4.35(t, 4H, JHH' = 6c/s), 3.0(S, 4H)

i.r. (Nujol Mull) : as chloride

2,2'-phenylenedioxy(bis)diphenylphosphinoethane (23)

Method 1: Via the ditosylate (21)

The ditosylate (21) (1.36g, 2.69 mmole) in T.H.F. (20 ml) was added dropwise (30 mins, 20°) to a stirred solution of lithium diphenyl phosphide (5.38 mmole, 30 ml T.H.F.). Solvent was removed in vacuo and afforded a pale yellow viscous oil. Recrystallization from boiling ethanol gave 2,2'-phenylenedioxy(bis)diphenylphosphinoethane, 0.88g, 61%, as a white crystalline solid (decomp. >120° in air) which was not air sensitive in the solid state.

For $C_{34}H_{32}O_2P_2$, mw 534.

calc: C, 76.4; H, 6.0; O, 6.0; P, 11.6.

Found: C, 77.0; H, 6.2.

^1H nmr. ($CDCl_3$): 2.55 (t,4H), 4.1 (m, 4H), 6.75(s, 4H), 7.3(br,s,20H).

i.r. (Nujol Mull): 1600(m-s), 1505(m), 1435(m), 1360(w), 1330(w), 1255(m-s), 1200-900 (very complex medium intensity bands closely similar to the diol), 825(m), 790(m), 740(s), 700(s), 670(m).

Method 2 via the dichloride (22)

The reaction between the dichloride (22) and lithium diphenylphosphide (prepared as previously described) was carried out by method A and gave an impure product shown by t.l.c. (silica gel, ether). n.m.r. and i.r. to contain 2,2'-phenylenedioxyl(bis)diphenylphosphinoethane. Further purification or characterisation was not attempted.

Section 2.4 References for Chapter 2

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CHAPTER 3

CHAPTER 3

PREPARATION AND PROPERTIES OF PHOSPHINO-ETHER CHELATE COMPLEXES

SECTION 3.1

Introduction

Whilst preliminary attempts to prepare macrocylic crown-phosphines were unsuccessful, the ready availability of the linear phosphino-ethers, $Ph_2PCH_2CH_2(OCH_2CH_2)_nPPh_2$ (hereinafter denoted as L_n where n = 1, 2 or 3), encouraged an investigation of their reactions with the group VIIIb transition metals, rhodium and iridium.

The coordination chemistry of mono-, bi- and polydentate phosphorus ligands has been extensively investigated and reviewed.[1,2] The main interest in ligands containing PX_3 donors (X = alkyl, aryl, alkoxy, halogen) arises from the well known observation that these donors show a marked preference for the heavy group VIII metals. As discussed in Chapter 1, phosphine complexes containing a transition metal with a d^8 configuration have been used in many synthetically and industrially important chemical reactions, e.g. :

(i) Catalytic reactions such as : homogeneous, hydroformylation, oxidation and hydrogenation or dimerisation of olefins.[3,4,5]

(ii) Oxidative addition reactions of protonic acids, alkyl or acyl halides, hydrogen halides, etc.[6]

(iii) Lewis basicity of metal complexes.[7]

(iv) The coordination of small covalent molecules.[8]

A common factor in all these reactions is the coordination of small molecular entities to the central metal atom. As discussed in Chapter 1, the stereochemistry and reactivity of the complex will be profoundly affected by the nature of the phosphine with regard to its basicity and imposed steric constraints. For example, the importance of chelation in changing both the stereochemistry and also the type and nature of complex formed is readily illustrated by the chemistry of the Rh(I) and Ir(I) complexes of triphenylphosphine, 1,2-bis(diphenylphosphino)-ethane or its methyl analogue, and the tridentate chelating phosphine $PhP(CH_2CH_2CH_2PPh_2)_2$. Such complexes have been the subject of intensive

investigation and are particularly well characterised due to the increasing tendency to use X-ray crystallography to determine the solid state structures.* For example, treatment of $RhCl_3 \cdot 3H_2O$ with Ph_3P gives the well known $RhCl(Ph_3P)_3$[5], whilst use of the chelating diphosphine, dme, gives a mixture of cis and trans cations $[Rh(dme)_2Cl_2]^+ Cl^-$.[10] Furthermore, treatment of $RhCl(Ph_3P)_3$ with dme in benzene displaces all the Ph_3P ligands, giving a very stable square planar d^8 cation, $[Rh(dme)_2]^+ Cl^-$.[10,11] A further example is given by the work of Ibers et al. who report the preparation, crystal structure and chemistry of $RhCl(PhP(CH_2CH_2CH_2PPh_2)_2)$, a square planar chelated analogue of $RhCl(Ph_3P)_3$.[9] The authors rationalised that the use of a chelating triphosphine should simultaneously accomplish:

(i) A more predictable coordination number and stoichiometry in the resulting d^8 complexes, as the chelate effect should minimise the tendency of one or more phosphino groups to be displaced during a chemical reaction.

(ii) More control on the stereochemistry of the complexes by using a chelating ligand.

The remarkable properties of $RhCl(PPh_3)_3$ for hydrogenation,[5] and $RhH(CO)(PPh_3)_3$[3,4] for hydroformylation of olefins, depend on the dissociation of Ph_3P ligands in solution.[12,12,2,59,60**] Accordingly, it is not surprising that no catalytic activity was reported for $Rh(Cl)(PhP(CH_2CH_2CH_2PPh_2)_2)$.[9] However, a marked increase in basicity (relative to $Rh(Cl)(Ph_3P)_3$ or trans-$Rh(Cl)(CO)(Ph_3P)_2$) was observed, as shown by increased oxidative reactivity towards small molecules such as CO, BF_3, SO_2, O_2 or S_2. This observation was not rationalised by the authors. However, crystal data[9] shows that whilst one axial coordination site in $Rh(Cl)(PhP(CH_2CH_2CH_2PPh_2)_2)$ is sterically hindered, overall there is probably less hindrance to incoming substrates than might be encountered in $Rh(Cl)(Ph_3P)_3$. Furthermore, the use of a chelating ligand gives good square planar geometry at the metal and very short Rh-P bonds (even when compared to Rh complexes of chelating ligands such as dPe*). Accordingly, both reduced steric hindrance to incoming substrates and possibly steric compression of the Rh-P bonds may be contributory factors to the apparent increase in basicity observed at Rh.

With these factors in mind it was hoped that L_n (n = 1, 2 or 3) could be used

* For examples see Chapter 4 and references therein.

** References 12 and 13 may need reinterpretation in the light of references 59 and 60.

to accomplish :

(i) An investigation of the effect of increasing chain length on the stereochemistry and nature of complexes formed with Rh(I) and Ir(I).

(ii) The possible production of complexes involving both soft P and hard O-donor bonds. In this context it is known that neutral ether bonds to group VIII transition metals are likely to be weak, this being borne out by the rarity of such complexes. Whilst the disposition of donors in L_n is at least superficially suitable* for them to behave as polydentate chelates involving M . . . O donation, such behaviour is unlikely to be observed unless additional stabilisation from chelation occurs. L_n can be used to gauge the extent and importance of such M . . . O interactions (if any) with a view to producing highly co-ordinatively unsaturated systems stabilised by the potentially reversible chelation of a weak O-donor. Such systems should have importance in catalysis.

(iii) Information gained on the nature of L_n donors should give insight into both the stereochemical requirements and chemistry of the macrocyclic phosphino-ethers and show whether further investigation into the synthesis of such ligands is worthwhile.

Possible Stereochemistry of Group VIII Metal Complexes of L_n

The effect of ring size on the stability of metal chelates has been much investigated and large chelate rings from flexible ligands were thought not to exist.[15] The stability associated with chelation has been regarded as an entropy or probability effect.[14,16,17] However, ring strain is likely to be less in large rings (12 to 15 atoms) than in rings of intermediate size, as in the cycloalkanes.[18] It has been suggested that large rings involving flexible bidentate ligands might be generally more stable than rings of intermediate size.[19] L_n acting as bidentate P-donors allow, in

* cf. the early transition metal complexes of the chelating N donors, trien and tetraen, reference 14

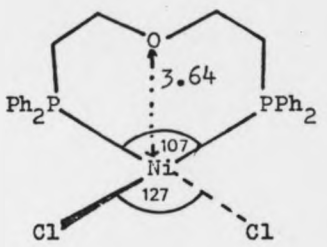
principle, the formation of 8, 11 and 14 membered chelate rings (for n = 1, 2 or 3). The introduction of heteroatoms in the ligand chain will further reduce ring strain[21] and increase the probability of observing both large and medium chelate rings.

L_1 and L_2 have previously been shown to form the chelate complexes, NiL_1Cl_2[21] (I) and NiL_2I_2[22,23] (II) and their structures (figure 3.1.1) have been completely established by X-ray methods.[21-23] We have found no other systematic use of L_n in the literature and these crystal structures afford valuable information on the steric and electronic behaviour of these ligands. (I) was found to be high spin and this, together with its spectroscopic similarity to $NiCl_2(Ph_3P)_2$, suggested a tetrahedral geometry. Similarly analogous pseudo-tetrahedral structures have been postulated for complexes of the diphosphine ligands 1,4-bis(diphenylphosphino)-butane and 1,5-bis(diphenylphosphino)-pentane with Co(II) and Ni(II) halides.[24] X-ray crystallography confirmed a distorted tetrahedral geometry for (I) with a P_2Cl_2 donor set. The P-Ni-P angle of 107°, together with a rather long Ni . . . O non-bonded contact of ca. 3.6 Å is believed to imply no significant Ni . . . O interaction. This contrasts with $NiI_2(Ph_2PCH_2CH_2SCH_2CH_2PPh_2)$[21] and $NiBr_2(Ph_2CH_2CH_2NCH_2CH_2PPh_2)$[25] for which spectroscopic evidence suggests square pyramidal five coordinate structures with the ligands acting as tridentate chelates and the softer N- and S-donors bonding to the metal The di-ether ligand complex (II) was low spin and therefore nominally square planar. Crystal data showed one of the largest distortions from square planarity ever observed for a Ni complex, with P-Ni-P = 162° and I-Ni-I = 143.5°. The ligand chain was disordered in the crystal state and refinement with two preferred, partially occupied sites for the chain, indicated that at its closest approach there were Ni . . . O non-bonded contacts of ca. 3.2 Å. It was postulated that this distortion towards tetrahedral geometry arose as a direct consequence of the Ni . . . O interaction preventing the opening of the P-Ni-P bond angle to the normal value of 180° expected for trans geometry.

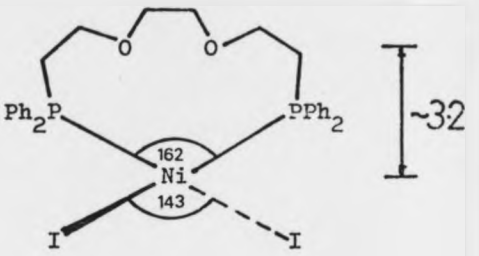
There are, as yet, no reports of flexible diphosphine ligands acting as trans bidentate donors to square planar rhodium atoms. However, Shaw et al. have recently reported[19] large ring chelate complexes of the ligands $R_2P(CH_2)_nPR_2$ (where R = Bu^t and n = 9, 10) with Pt and Ir (figure 3.1.1). Here the ligands function as trans bidentate donors, forming monomeric complexes (III, IV), and also as bridging ligands in dimeric species (V).

It is clear that L_n should be capable of functioning as trans bidentate donors

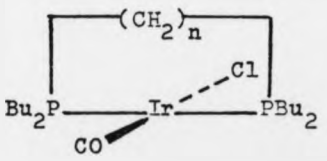
Figure 3.1.1.



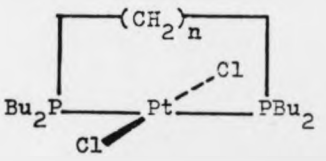
NiL1Cl'2 (I)



NiL2I2 (II)



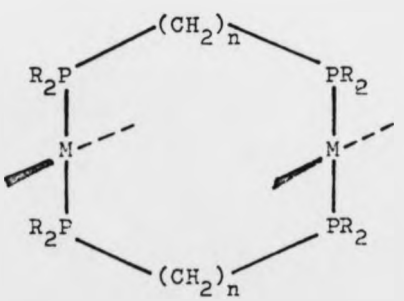
(III)



(IV)

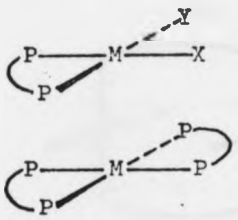
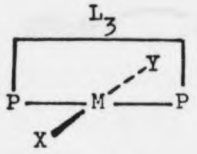
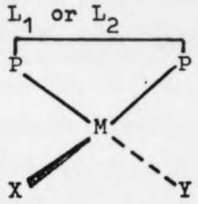
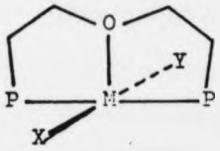
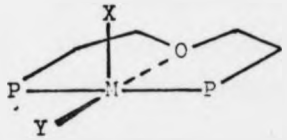
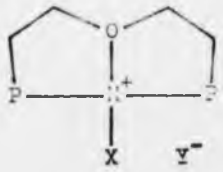
M=Ir or Pt

n=9 or 10



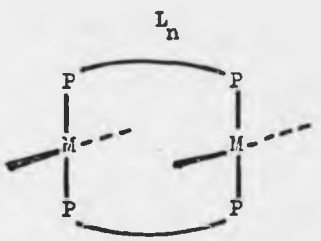
(V)

Figure 3.1.2. Possible Stereochemistry of L_n Complexes of Group VIII Metals.

Projected L_n Complex	Evidence
	The P-M-P angle of 107^0 observed in NiL_1Cl_2 shows that L_1 could function as a cis donor.
	This type of geometry is post-ulated for $IrCl(CO)(Bu_2P(CH_2)_9PBu_2)$ See figure 3.1.1.
	The observed geometry in NiL_2I_2 See figure 3.1.1.
	Square pyramidal adducts are postulated for $Ni(PSP)I_2$ and $Ni(PNP)Br_2$, see text.
	
	The ligand might exhibit the type of geometry observed in the complex $Ni(PNP)Br_2$

Substituents on phosphorus are omitted for clarity.

Figure 3.J.2. continued.

Projected L_n Complex	Evidence
	Observed in Pt and Ir complexes of $Bu_2P(CH_2)_nPBu_2$, for n: 9 or 10 . See figure 3.I.I.
XYZ-M-P P-M-XYZ	Oligomeric or polymeric complexes are frequently formed with poly--dentate ligands, for example $(Rh(CO)_2Cl)_2dPm$.

in Rh(I) and Ir(I) complexes. Furthermore, the X-ray data on NiL_nCl_2 (I, II) demonstrates the importance of M . . . O interactions in determining the final stereochemistry. It is possible that the extent of these interactions may be so balanced as to depend markedly on the metal oxidation state. Figure 3.1.2 suggests schematically the extremes of geometry which might be encountered for Rh(I) and Ir(I) complexes of L_n, together with such evidence as is available for the proposed structures.

Possible Synthetic Routes to L_n Complexes of Rh and Ir

There are a large number of d^8 complexes of Rh and Ir for which the synthesis of L_n analogues might be attempted. Suitable and extensively investigated examples are trans $MCl(CO)(Ph_3P)_2$[26-30] (VI), trans $MCl(C_2H_4)(Ph_3P)_2$[5,31] (VII) and $MCl(Ph_3P)_3$[5,32,33] (VIII) where M = Rh, Ir. More recently, stable and isolable cationic solvates of the type $RhCO(Ph_3P)_2(S)^+$ (IX) where S = acetone, acetonitrile, d.m.f., etc., have also been prepared.[34] Accordingly, synthetic routes to L_n analogues of (VI), (VII) and (IX) were envisaged as shown in figure 3.1.3. Initial attempts (route A) were directed towards the production of trans $RhL_n(Cl)(CO)$ (X), this being dictated by the following considerations :

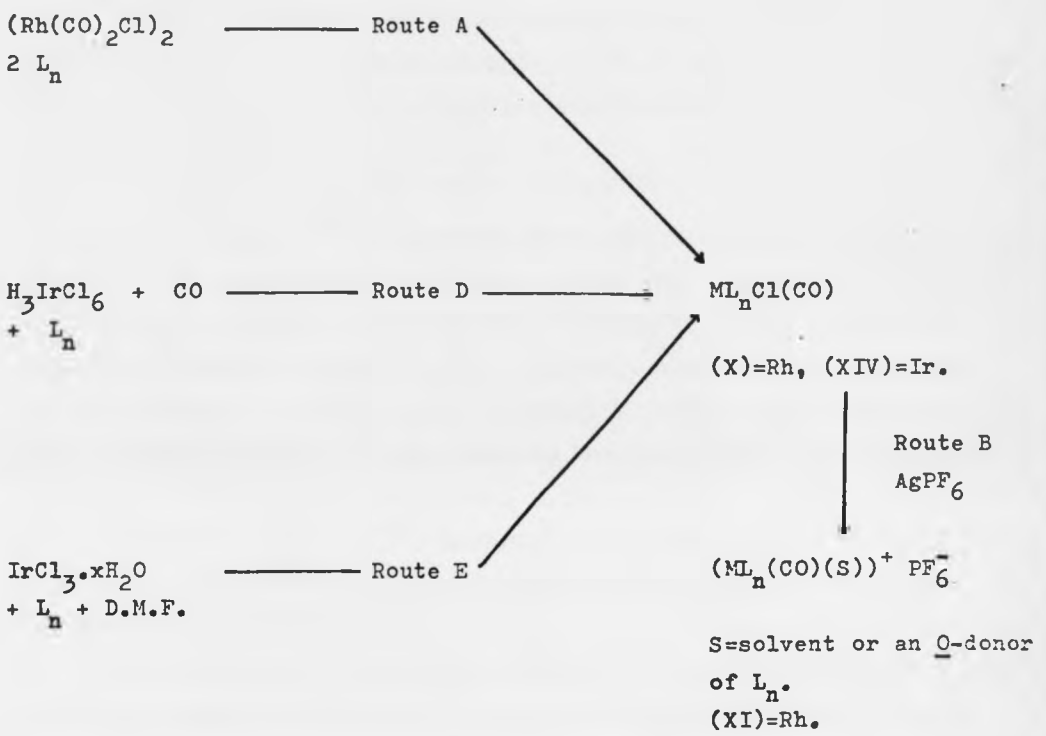
(i) Shaw et al. have already demonstrated[19] that similar Ir(I) chelates (III) may be prepared.

(ii) The known stability of (VI), its low oxidative reactivity and the clean synthetic route available via CO displacement from $(Rh(CO)_2Cl)_2$[26] maximise the possibility of obtaining good yields of the L_n analogue (X). This is important since Shaw has reported[19] considerable difficulty in separating mixtures of products obtained in the synthesis of (III).

(iii) The vibrational spectra of CO complexes afford a valuable indication of the purity, structure and oxidation state.

(iv) Treatment of (VI) with $AgPF_6$ readily affords cationic complexes of the type $[RhCO(Ph_3P)_2(S)]^+ PF_6^-$ (IX).[34] The analogous L_n complex (XI) should be accessible (route B) and the increased 'hard acid' character of the cation should favour hard ether O-donation from the chain.

Figure 3.1.3. Possible Synthetic Routes to L_n Complexes of Rhodium and Iridium.



$(M(C_2H_4)_2Cl)_2 + 2\ L_n \xrightarrow{\text{Route C}} 2\ ML_n(Cl)(C_2H_4)$

(XII)=Rh, (XIII)=Ir.

Where L_n is $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ and n=1,2 or 3.

Subsequently a preliminary investigation into Rh and Ir ethylene complexes (XII) and (XIII) and the Ir carbonyl complex (XIV) was carried out (routes C, D, E) and demonstrates considerable differences in reactivity.

SECTION 3.2

Preparation and Reactions of Neutral Rhodium Carbonyl Complexes of L_n

Vallarino[26] demonstrated that the reaction of Ph_3P with $[Rh(CO)_2Cl]_2$ gave excellent yields of trans $Rh(Cl)(CO)(Ph_3P)_2$ via CO displacement and subsequent chloride bridge cleavage. This complex has been characterised

$$[Rh(CO_2)Cl]_2 + 4\,Ph_3P \xrightarrow{20^\circ} 2\,\underline{trans}\ Rh(Cl)(CO)(Ph_3)_2 + 2\,CO$$

by X-ray crystallography.[35] A number of short chain (3, 4 or 5 atom) diphosphines readily undergo similar reactions, giving cis monomers, oligomers or polymers. For example, the monomethylenediphosphine $Ph_2PCH_2PPh_2$ (dPm) gives a mixture of products on reaction with $[Rh(CO)_2Cl]_2$ including a monomeric chelate complex, $[RH(CO)Cl(dPm)]$, a bridged dimer, $[[Rh(CO)_2Cl]_2 \cdot dPm]$, and an oligomeric complex, $[Rh(CO)Cl(dPm)]_n$.[36] Much less ring strain is involved in a cisoid chelate complex of $Ph_2PCH_2CH_2PPh_2$ (dPe), which, in the same reaction, readily forms the well known cation $[Rh(dPe)_2]^+\ Cl^-$.[37] Similarly, the ligand $Ph_2PCH_2 \cdot O \cdot CH_2PPh_2$ (POP) is reported to give largely cationic species in solution, and $[Rh(POP)_2]^+$ may be isolated as its BF_4^- salt.[36]

We were interested in the behaviour of L_n (n = 1, 2 or 3) which have not been previously reacted with $[Rh(CO)_2Cl]_2$, since these represent a graded series of electronically very similar ligands capable of forming 8, 11 and 14 membered chelate rings. In the following section (3.2.1) the reaction of L_1 is considered. L_1 (7 chain) is particularly interesting since it is neither short enough to form undistorted cis complexes, nor long enough to bond undistorted trans. Furthermore, on the basis of the NiL_1Cl_2 structure discussed in section 3.1, Rh . . . O interactions may be important in chelate complexes of this ligand.

3.2.1 The Preparation and Reactions of $RhL_1(Cl)(CO)$, (1)

1,5-bis(diphenylphosphino)-3-oxa pentane (L_1) displaces CO from tetracarbonyl dirhodium dichloride in MeOH (0^o) forming an oily yellow precipitate which, after recrystallisation from CH_2Cl_2/MeOH gave a crystalline yellow solid analysing for $RhL_1(Cl)(CO)$ (1), figure 3.2.1. The reaction is both solvent and temperature dependent, a mixture of products resulting (as shown by additional i.r. bands at 1990, 2010, 2040, 2100 cm^{-1}) either when both substrates and products are soluble (as in benzene, CH_2Cl_2 or Et_2O) or at temperatures above 30^o. CO is firmly bound since (1) does not react with a further mole of L_1 in CH_2Cl_2 or with ca. 10M excess of Ph_3P or tri-isopropyl phosphine in benzene. (1) is air and moisture stable, will not reduce $AgNO_3$, is unaffected by 50% aqueous H_2SO_4 or HCl, and closely resembles trans $Rh(Cl)(CO)(Ph_3P)_2$ in chemical and physical properties.[26]

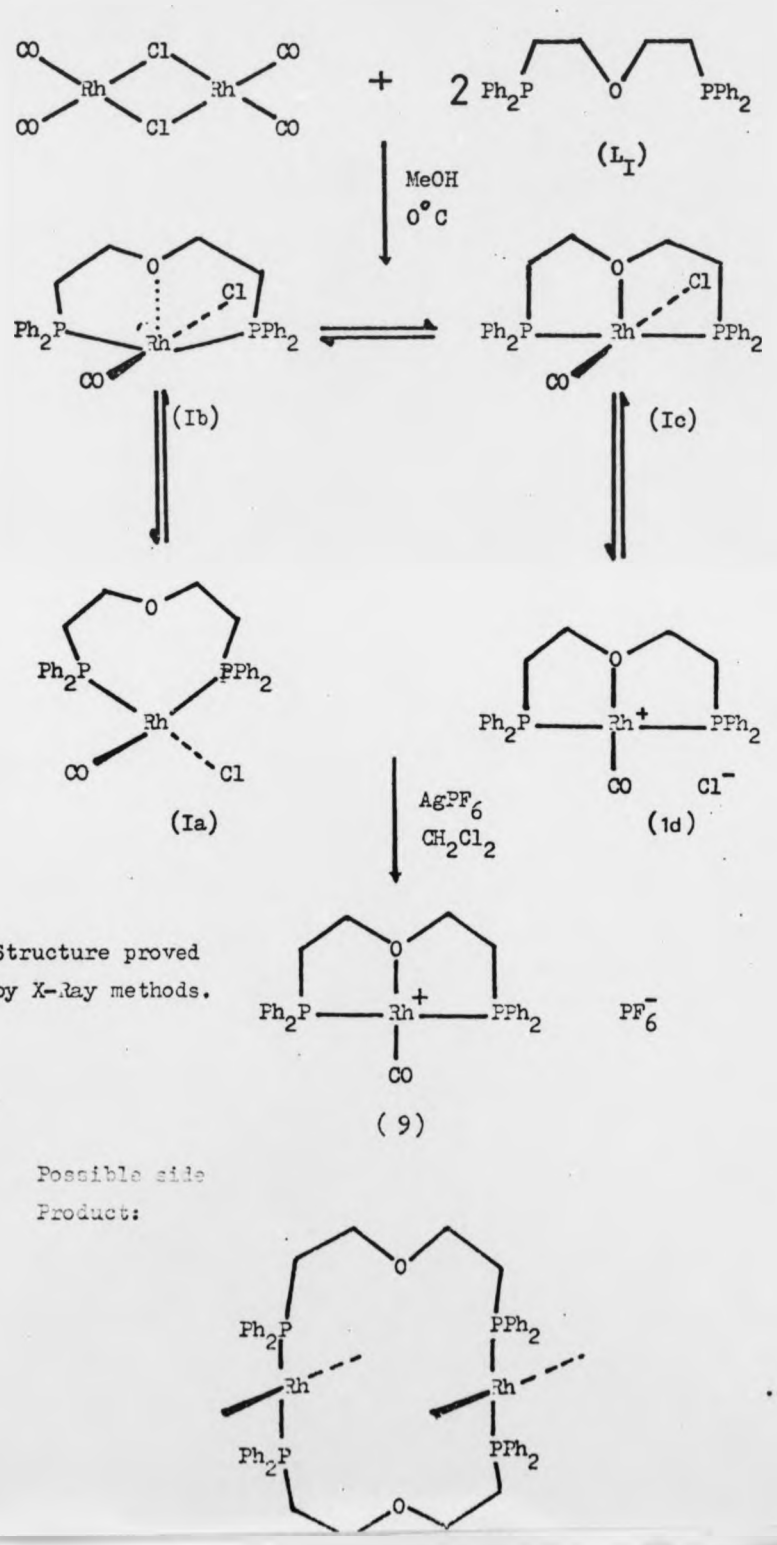
Figure 3.2.1 shows schematically possible geometries consistent with the empirical formula (see section 3.1). Crystal data for NiL_1Cl_2[21] and $[RhL_1CO]^+ PF_6^-$* show that L_1 acts as a bidentate P donor in the former (distorted tetrahedral geometry with P-Ni-P = 107^o) and as a tridentate donor with trans P and cis O donors in the latter (in plane, distorted square planar geometry with P-Rh-P $\simeq 166^o$). Accordingly, structures lying between these extremes (1a - 1d) were considered and the possibility of an equilibration between such species in solution exists, figure 3.2.1.

Conductivity was typical of a neutral complex (Λ_m = 13.9, acetone, 25^o, 10^{-3} M solution)** and consequently major contributions of cationic structures (1d) may be ruled out. Similarly, the low oxidative reactivity of trans $Rh(Cl)(CO)(Ph_3P)_2$ infers that five coordinate O-bonded complexes such as (1c) are chemically unlikely. The u.v./vis. spectrum (λ_m = 364 n.m. ϵ_m = 3230) resembles that of the known complexes trans $M(Cl)(CO)(Ph_3P)_2$ where M = Rh, Ir. This, together with the conductivity data suggests that Rh . . . O interactions are not a dominant feature of (1).

Spectral data is presented in figure 3.2.2. The i.r. spectrum is unremarkable, showing the expected ligand absorptions to be unshifted on complexation. The carbonyl stretching frequency [ν(CO)= 1975 cm^{-1}. CH_2Cl_2, and 1965 cm^{-1} nujol] was in the range expected for a trans adduct [cf. trans $Rh(Cl)(CO)(Ph_3P)_2$, ν(CO) = 1965 cm^{-1}, nujol, and cis $Rh(Cl)(CO)(Ph_2PCH_2CH_2PPh_2)$, ν(CO) = 2010 cm^{-1}].[49]

* This work, Chapter 4
** Ref. W. J. Geary, Coord.Chem.Reviews, 1971, 7, 81.

Figure 3.2.I



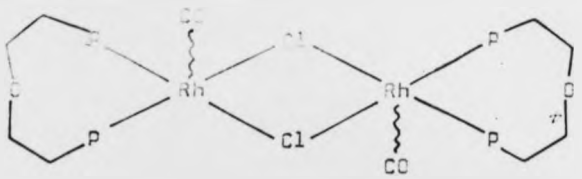
Structure proved by X-Ray methods.

Possible side Product:

^{1}H n.m.r. was characteristic of a fluxional system showing broad peaks corresponding to the methylene protons at C(1) and C(2). Cooling to -85° resulted in further slight broadening but no evidence of fine coupling or of new peaks corresponding to isomeric products was observed. Similarly, ^{31}P spectra* showed the expected[41] doublet for two identical P atoms coupled to Rh with J(Rh-P) = 125.0 c/s (cf. J(Rh-P) = 129 c/s in trans $RhCl(CO)(PPh_3)_2$). The ^{1}H n.m.r. spectrum of a coordinated diphosphine will differ from that of the uncoordinated ligand[38,39] in that the magnetic equivalence of some protons may change and the extent of shielding will change. Furthermore, the coupling between P and the protons will depend upon the stereochemistry of the complex. Figure 3.2.3. compares this data for L_1, complex (1) and $[RhL_1CO]^+PF_6^-$, (9). The near equivalence of chemical shifts in (1) and (9) reflects a similar magnetic environment for L_1 in both complexes. In particular, the large shift, on complexation, for the protons at C(2), implies that in (1) the ligand chain is also, on average, close to the metal atom. The lack of fine coupling in (1) suggests that the chelate ring is non-rigid and therefore a strong Rh-O bond is absent. It is thought that the structure lies between the extremes of tetrahedral (1a) and five coordinate (1c) geometry.

Cryoscopic molecular weight determinations in benzene on 10^{-3}M solutions of (1) gave average values of 711 and 697, for two successive solutions. The average value of 704 is somewhat higher than monomer (608.5) but too low for dimer (1217.0), or higher oligomers. This data is consistent with (1) being predominantly monomeric in solution (unfortunately the complex is involatile (200°, 10^{-3} mmHg) and gives no evidence of molecular ions in the mass spectrum). The high value observed for the cryoscopic molecular weight could be interpreted in terms of extensive dissociation of a dimer to a monomer. Two possible dimers are envisaged :

(i) A five coordinate chloro-bridged dimer of the type shown below :



* Unfortunately the necessary calibration capillaries and centering formers were not available at the time of this study. The loss of ^{31}P chemical shift data is regretted.

A structure of this type is perhaps somewhat unlikely in view of the known chemistry of trans-$Rh(Cl)(CO)(Ph_3P)_2$, which is not reported to form dimers of this type.

(ii) A four coordinate phosphine-bridged structure of the type shown in figure 3.2.1. This is both sterically and electronically a more reasonable possibility. Furthermore nucleophilic attack at Rh by the O-donors of L_1 might promote facile dissociation to give monomeric species.

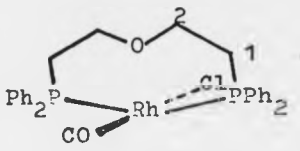
Finally, it is noted that an equilibrium between monomeric and dimeric species might explain the broadening of the ^1H n.m.r. peaks and resulting loss of fine coupling.

Note Added in Proof* Slow evaporation of a saturated CH_2Cl_2 solution of (1) gives a related macrocrystalline product. Preliminary results of a crystallographic determination of the structure of this material indicate that it may have the phosphine-bridged dimeric structure shown in figure 3.2.1. The ^1H n.m.r. of this material (recorded immediately after preparation of the solution in $CDCl_3$) is identical with that of (1), implying very rapid dissociation to monomer. (* Private communication from Drs. N. W. Alcock and J. M. Brown).

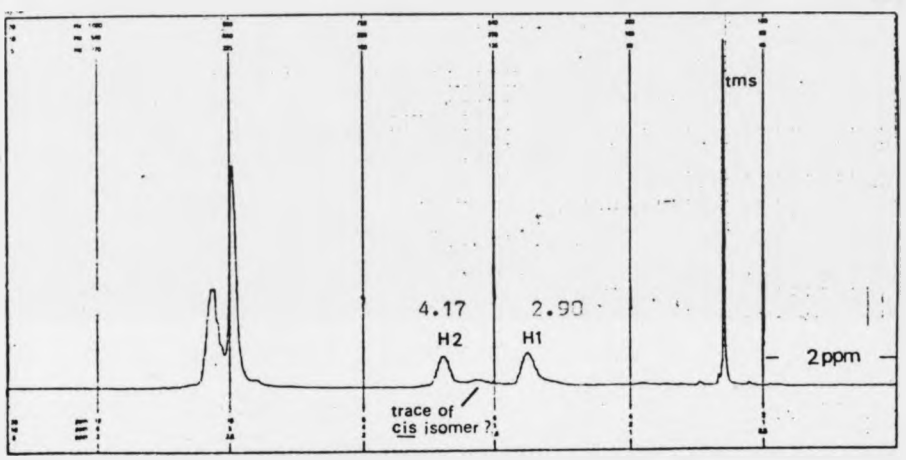
Evidence of Different Products (Possibly Isomeric) in Freshly Prepared $RhL_1(Cl)(CO)$

The ^1H n.m.r. spectrum of freshly precipitated (1), which had not been recrystallised or allowed to stand in solution, showed evidence of isomeric products. Figure 3.2.4 shows schematically the ^1H n.m.r. spectra of a freshly prepared $CDCl_3$ solution of (1) and that obtained on standing the same solution several minutes at 20^o, together with tentative structures of possible isomers involved. The spectrum of the fresh solution shows the expected methylene resonance for C(1). However, there are two peaks corresponding to the protons at C(2) with total integral equivalent to four protons. After standing for 10 minutes the peak at 3.68 has dissappeared with

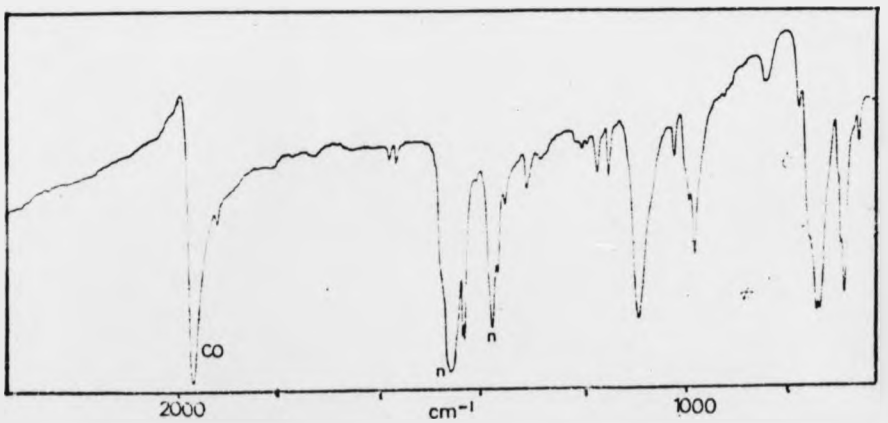
Figure 3.2.2. Spectral Data for $RhL_4Cl(CO)$.



(1)

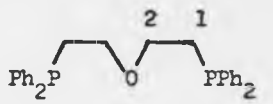


^1H n.m.r. of (1) in $CDCl_3$ at 300°K, referenced against t.m.s. =0 p.p.m.(1 large division=2 p.p.m.).

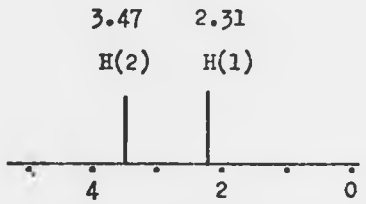


I.r. (Nujol) of (1). Nujol peaks= n.

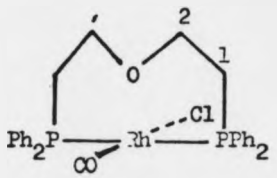
Figure 3.2.3. Comparison of ^1H n.m.r. Spectra for L_1, (1) and (9).



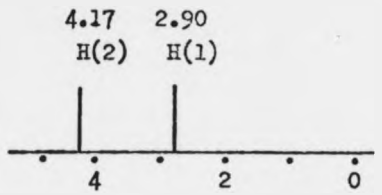
(L_1)



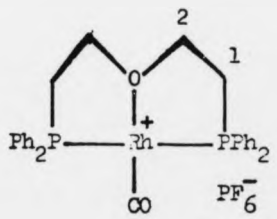
multiplets



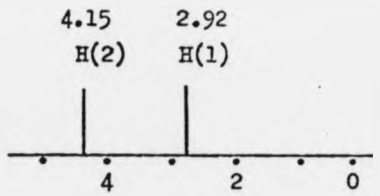
(1)



broad singlets



(9)



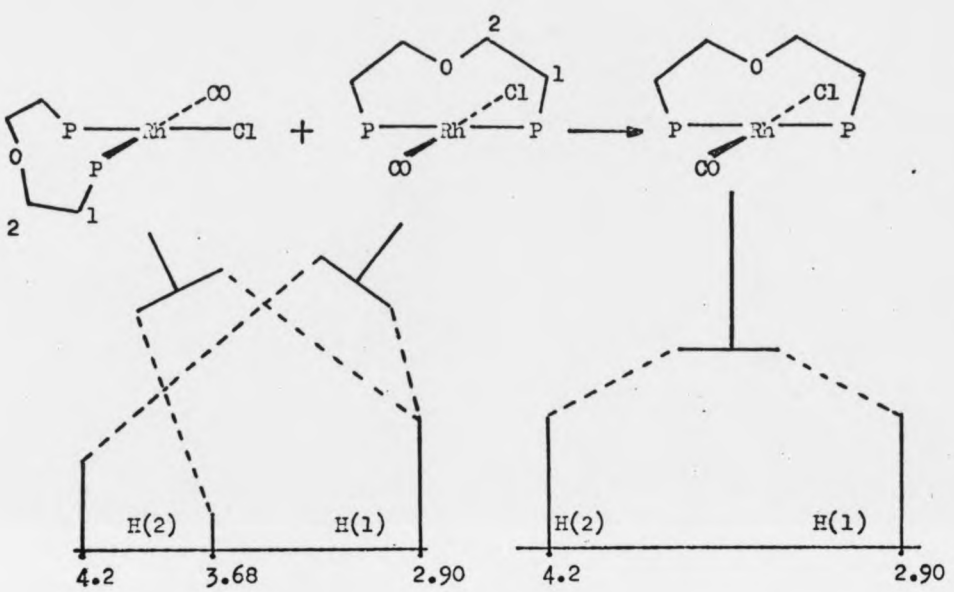
multiplets

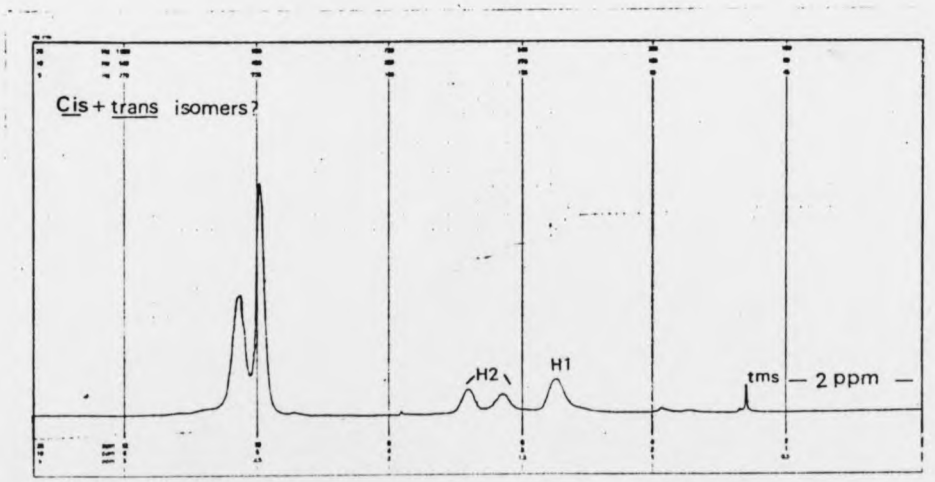
Structure established by X-Ray crystallography

Spectra were run in $CDCl_3$ with t.m.s. as internal reference, δ t.m.s.: 0 p.p.m.

Full spectral details appear in text.

Figure 3.2.4. A Possible Isomerisation Reaction of $RhL_1(Cl)(CO)$





^1H n.m.r. spectra were run as solutions in $CDCl_3$ with t.m.s. as internal reference (δ t.m.s. :0 p.p.m.).

concomittant increase in intensity of the peak at 4.20, the final spectrum being that of the recrystallised material. It will be shown* that the methylene protons at C(2) and C(2)' in the O-bonded cation $[RhL_1CO]^+ PF_6^-$ (9) are rapidly equivalenced by inversion and that this obtains to -80^o. It is therefore unlikely that L_1 in any trans conformation (with or without Rh - O bonding) could explain the observed splitting of the C(2) methylene signal. A facile explanation of this behaviour might be the existence of some cis isomer in the freshly precipitated product and that rapid isomerisation to the more stable trans isomer occurs in solution. Some support for this belief is given by the close similarity of the "cis" C(2) chemical shift (3.68 p.p.m.) with that of the free ligand (3.47 p.p.m.). In NiL_1Cl_2[21] the C(2) methylene groups are well removed from the metal atom and this is likely to be the case in any cis $RhL_1(Cl)(CO)$. Modification of the magnetic environment of C(2) protons via Rh . . . O or through space interaction will therefore be smaller than in a trans isomer, as is observed. Nujol mulls of the isomeric mixture show a somewhat broadened ν(CO) resonance with strong asymmetry towards low wavenumber; this may conceal cis ν(CO).

Four Coordinate Derivatives of $RhL_1(Cl)(CO)$

Vallarino[26] reported that trans $Rh(Cl)(CO)(Ph_3P)_2$ undergoes slow exchange reactions with lithium halides (Br or I) to give the corresponding bromo and iodo derivatives. Similarly, reaction with NH_4SCN was reported to give trans $Rh(CO)(Ph_3P)_2(NCS)$. Any tendency for (1) to form cationic O-bonded derivatives such as (1d), even if in very small equilibrium concentration with neutral species, might lead to greatly increased exchange rates. No such behaviour was observed for (1), confirming the belief that O-donor interaction is slight. $RhL_1(Br)(CO)$ (2) was prepared by refluxing (1) with a 10M excess of NaBr in acetone/CH_2Cl_2. Exchange is slow and the yellow solid (2) obtained on Et_2O extraction gave rather poor analytical figures. The i.r. spectrum was identical to (1) apart from loss of $\nu(Rh-Cl) = 300\ cm^{-1}$ as expected† and readily attributable to ν(Rh - Br) was observed at 220 cm^{-1}. The bromide complex was also prepared by in situ conversion of $[Rh(CO)_2Cl]_2$ to the bromide by refluxing with a twenty-fold molar excess of LiBr prior to addition of L_1 to the cooled solution. $RhL_1(CO)(I)$ (3)

* This work, section 3.3.1.

† ν(Rh - Br) and (Rh - I) are reported to lie below 200 cm^{-1} in complexes of this type.[40]

could not be isolated pure. Reaction of (1) with a ten-fold molar excess of LiI in acetone/CH_2Cl_2 gave an intractable mixture of products. Recrystallisation from EtOH/CH_2Cl_2 afforded a deep yellow solid (3) in low yield with i.r. spectrum similar to (1) (3,000 - 400 cm^{-1}) but this gave very poor analytical figures. Replacement of chloride by iodide should be a facile process, although difficulty has often been reported in the preparation of iodo-organometallic compounds (cf. $Rh(I)(Ph_3P)_3$[5]). A benzene solution of (3) appeared to oxidise on standing in air (24 hours) affording a pale brown solid. This showed a new i.r. band at 885 cm^{-1} (nujol), possibly attributable to a $Rh-O_2$ adduct.[48] $RhL_1(CO)(\underline{N}CS)$, (4). Treatment of $RhL_1(Cl)(CO)$ with NH_4SCN (acetone/Et_2O, 35 mins., 20°) gave a yellow precipitate analysing for $RhL_1(CO)(\underline{N}CS)$, (4). The ^1H n.m.r. and i.r. spectra were very similar to those of (1) apart from new i.r. bands at 2085 (s, sharp), 2005 (s, sharp), 1985 (s) and 840 (m) cm^{-1}.

Bonding in transition metal thiocyanate complexes is a matter of considerable current interest as witnessed by a recent and comprehensive review by Norbury[42a] which lists over 800 references. The thiocyanate ion is an ambident ligand that can coordinate either through the sulphur or nitrogen atom and can also function as a bridging ligand. This ambident behaviour can be partially interpreted in terms of the hard/soft concepts of Pearson.* In complexes of Class B or soft metals, such as Pd(II) or Pt(II), coordination is expected to occur through the soft sulphur atom.[43a] Whilst this general pattern appears to hold, a large number of exceptions exist. It is clear that for many mixed ligand complexes a subtle balance exists between electronic, steric and solvent effects. It has been concluded that if either the steric or electronic factors of a series of complexes are held constant, it is often possible for the other factor to determine the nature of the linkage isomer which results.[42a]

An excellent example of steric control is the change of coordination observed along the series $\underline{cis}$-$Pd(L_1)(\underline{S}CN)_2$, $\underline{cis}$-$Pd(L_2)(\underline{S}CN)(\underline{N}CS)$, $\underline{cis}$-$Pd(L_3)(\underline{N}CS)_2$, where $L_n = Ph_2P(CH_2)_nPPh_2$ for n = 1, 2 or 3.[43a] As previously noted*, increasing the size of the chelate chain increases steric hindrance at the thiocyanate coordination sites, thereby causing the observed change from bent

* See Chapter 1, section 1.1

S- to linear N-bonding. Palenik et al.[43a] have implied that steric effects may, in general, be very important in thiocyanate complexes of Pd(II). The degree of importance has been questioned by other workers.[43b] It is not possible to rationalise the formation of N-bonded thiocyanates of other soft transition metals using only steric arguments. As originally pointed out by Turco and Pecile,[44a] the cooperative effect of the other donor ligands is also important. This has been rationalised on the basis of π-bonding,[44b] polyelectronic perturbation theory[42a] and the so-called antisymbiosis arguments.[44c] The nature of the solvent may also be important.[42b] Such 'explanations' are restricted to rather limited classes of compounds. Norbury's approach based upon polyelectronic perturbation theory appears to have widest generality, and also explains some of the solvent dependence observed. A tentative summary of this treatment is given below.

Cooperative Ligand and Solvent Effects in Thiocyanate Coordination

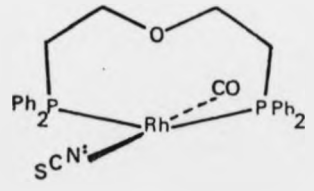
Metal	σ-donor ligand	Solvent		π-acceptor ligand
		High dielectric	Low dielectric	
Class A	-NCS	-NCS	-SCN	-SCN
Class B	-SCN	-SCN	-NCS	-NCS

Here a solvent effect is only expected for intermediate ligand situations and the use of terms such as σ-donor and π-acceptor is descriptive (in the hard/soft sense) rather than implying an understanding of the effect. It is also assumed that steric effects can completely override the solvent or even the ligand effects. Interestingly, both the hardest systems (Class A metals with σ-donor ligands such as amines) and the softest systems (Class B metals with π-acceptor ligands such as phosphines) are predicted to give N-bonded thiocyanates, whilst intermediate systems are S-bonded.

For the metal complexes of interest in this study, $Rh(L_1)(CO)(NCS)$, (4), the perturbation treatment predicts N-bonding. In support of this prediction N-bonding is observed for the complexes trans-$M(PPh_3)_2(CO)(NCS)$, (M = Rh, Ir),

a fact which has been rationalised on the basis of the strong π-bonding effect of the trans CO group.[44b] Similarly, $Rh(PPh_3)_3(\underline{N}CS)$ is N-bonded but it is not clear why in the complexes $Rh(PPh_3)_2(L)(CNS)$*, the N-bonded isomer is obtained for L = aniline or pyridine, whilst the S-bonded isomer is obtained when L = CH_3CN, Me_2CO or Et_2O.[42a] On balance both perturbation and π-bonding theories predict that (4) should be N-bonded. It is difficult to assess the importance of additional steric effects. Models suggest that (4) will be at least as sterically hindered as the complexes $M(PPh_3)_2(CO)(\underline{N}CS)$, (M = Rh, Ir), which also should favour N-bonding

Several authors[44] have shown that the C-S stretching frequency may be used diagnostically to distinguish between these possibilities, being shifted to higher wavelength for M-N and lower wavelength for M-S bonding (free KSCN = 749 cm^{-1}). On this basis (4) is assigned* the N-bonded isothiocyanate structure shown, the bands at 2085 and 840 cm^{-1} being the C-N and C-S stretches (cf. $Rh(CO)(PPh_3)_2(\underline{N}CS)$[26]). There is an unexplained band at 2005 cm^{-1} whose relative intensity is unchanged under varying reaction conditions and on re-crystallisation (CH_2Cl_2/Et_2O).



(4)

* This agrees with the work of Turco and Pecile[44a] who suggest that π-bonding ligands such as phosphines will favour the 'hard' M-NCS bond.

This is neither readily attributable to an impurity (cf. free NH_4SCN : $\nu(C-N) \sim 2020$ cm^{-1}) nor is it in the range expected for the S-bonded isomer ($\nu(C-N) > 2100$ cm^{-1}). Since all other data is in excellent agreement with the proposed trans isothiocyanate structure, this band is considered anomalous, possibly arising from an unexpectedly strong overtone or splitting of the CO band.

Oxidative Addition Reactions of $RhL_1(Cl)(CO)$

Square planar rhodium (I) compounds of general formula trans $Rh(Cl)(CO)(L)_2$ show no marked tendency towards oxidative addition reactions. For example, whilst oxidation does occur with halogens[26, 27] giving octahedral rhodium (III) complexes $RhClX_2(CO)(L)_2$ (X = Cl, Br, I; L = Ph_3P, $P(n-C_4H_9)_3$, or $P(C_2H_5)_3$), and with SO_2 to give the tetragonal adduct $Rh(Cl)(CO)(Ph_3P)_2SO_2$,[45] no isolable adducts are obtained on reaction with H_2, HX (X = Cl, Br or I), O_2 or CO. In contrast, the more 'basic'* iridium (I) carbonyl complex, $Ir(Cl)(CO)(Ph_3P)_2$ is oxidised not only by halogens, but also by a variety of other small molecules such as HX, X_2, CH_3I (X = Cl, Br or I), to give octahedral Ir(III)[27-30] adducts. The oxidative reactivity of (1) should be very similar to that of $Rh(Cl)(CO)(Ph_3P)_2$ unless significant steric hindrance or O-donation from the ligand chain becomes important.

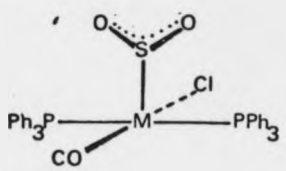
A CH_2Cl_2 solution of (1) did not react** with H_2 or CO (1 a.p. gas) as monitored by i.r. or u.v./vis. solution spectra, nor was any reaction observed with MeI (10 M excess in benzene or CH_2Cl_2).

$RhL_1(Cl)(CO)(SO_2)$ (5). A stable SO_2 adduct (5) could not be isolated establishing that the reactivity of (1) is lower than in the corresponding $Rh(Cl)(CO)(L)_2$ (L = Ph_3P) complex.[45] (5) is formed reversibly when gaseous SO_2 is bubbled through a solution of (1) in CH_2Cl_2 at 20° and ambient pressures. Removal of CH_2Cl_2 and SO_2 in vacuo or flushing the CH_2Cl_2 solution with N_2 gas affords unchanged (1). An i.r. solution spectrum of the CH_2Cl_2 equilibrium mixture shows unshifted bands due to (1) and four additional bands characteristic of (5). The carbonyl stretching frequency ($\nu(CO) = 2030$ cm^{-1}) is as expected for a five coordinate adduct (cf. trans $Rh(Cl)(CO)(Ph_3P)_2(SO_2)$, $\nu(CO) = 2034$) and the bands at 1060, 1190 and 1220 cm^{-1} are the symmetric and antisymmetric S-O stretching vibrations of an S-bonded SO_2 group.[9] Thus, (5) is formulated as shown, involving Rh ← S electron donation and

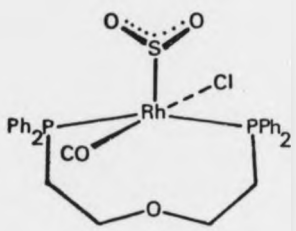
* Lewis basicity as defined in reference

** Within the limits of macroscopic detection.

bonding similar to that observed in the tetragonal complexes M(Cl)(CO)$(Ph_3P)_2(SO_2)$, M = Rh, Ir.[46,47] It is not geometrically possible for L_1 to act as a trans bidentate donor across the base of a tetragonal pyramid without chain O donating to the metal. It is believed that the actual structure lies between the extremes of tetragonal and bipyramidal geometry.



M = Rh, Ir.



(5)

The equilibrium constant for this reaction has not been determined; however, dissolution of (1) in neat liquid SO_2 and removal of SO_2 with a stream of N_2 gas at 0^o, afforded a yellow green solid shown by i.r. (nujol mull) to be substantially the SO_2 adduct (5). This rapidly lost SO_2, even at 0^o, giving unchanged (1) in contrast to Rh(Cl)(CO)$(Ph_3P)_2(SO_2)$ which is stable at 20^o.[45] The observed destabilisation of (5) may either arise as a result of non-bonded interactions from the ligand chain or SO_2 dissociation might be facilitated by M . . . O donation.

Collman et al.[47] treated Rh(Cl)(CO)$(Ph_3P)_2$ with O_2 and SO_2 under pressure in the hope that irreversible sulphate formation might intercept a rhodium-oxygen complex present in small concentration. However, they observed no such reaction and in agreement with their work we find that (1) shows no tendency to form a sulphate when reacted with oxygen in liquid SO_2 at ambient pressures.

The Reversible Reaction of (1) with HCl

Passage of dry HCl gas through a solution of (1) in CH_2Cl_2 at 20^o showed evidence of equilibrium uptake of HCl as monitored by both i.r. and u.v./vis. solution spectroscopy. No stable HCl adduct could be isolated, but a saturated solution of (1) in CH_2Cl_2 saturated with HCl at -80^o, gave white crystals. These decomposed rapidly

on filtration, affording unchanged (1). I.r. of a CH_2Cl_2 solution of (1) with approximately one hundred-fold molar excess of HCl showed ν(CO) = 1975, 2070 cm^{-1} and unshifted L_1 bands. ν(Rh - H) was either a very weak peak at 2200 or a medium peak at 2100 cm^{-1}. The bands at 2200, 2100 and 2070 cm^{-1} disappeared on N_2 degassing.

The u.v./vis. spectrum of a CH_2Cl_2 solution of (1) before and after the addition of ca. one thousand-fold molar excess of dry HCl is shown in figure 3.2.5. Loss of (1) may be correlated with loss of the band at λ_m = 364 nm and loss of ν(CO) = 1975 cm^{-1}. Accordingly, an estimate of K for the reaction :

$$(1) + HCl \xrightarrow{K} Rh\,L_1(Cl)(CO)(HCl) \quad (6)$$

was obtained by monitoring the absorption at 364 nm for known equilibrium mixtures of reactants. A value of K = 14 $\pm$ 1 was obtained and checked by an order of magnitude estimation based on ν(CO) in the i.r. (K $\approx$ 10 by this method). On the basis of the limited data available the nature of the HCl adduct is uncertain and figure 3.2.5 suggests possibilities, although no specific cis or trans addition products are implied. The u.v./vis. spectrum of (6) is similar to that of the known octahedral adduct Ir(Cl)(CO)$(Ph_3P)_2$(HCl). However, examination of molecular models shows that the analogous structure (6a) is sterically rather unlikely. Whilst five coordinate cations such as (6b) are not unknown, these are usually associated with complexes of high Lewis basicity.[9] The O-bonded structure (6c) is attractive in view of the spectral similarity of HCl saturated solutions of (1) and $[Rh\,L_1CO]^+PF_6^-$,* the HCl adduct $[Rh\,L_1(CO)(HCl)]^+PF_6^-$ being thought to have the O-bonded structure shown.

Treatment of (1) with O_2

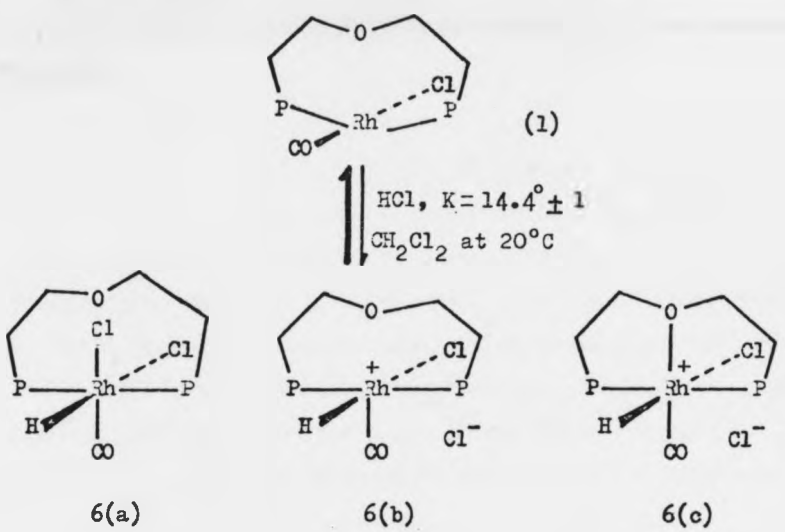
(1) does not appear to react readily** with O_2 to form either mono or dinuclear complexes, reflecting the known stability of Rh(Cl)(CO))$Ph_3P)_2$.[26] Treatment of (1) in benzene with dry O_2 for three days did give approximately 5% of a beige insoluble product, which could not readily be identified. Removal of benzene from the filtrate in vacuo gave unchanged (1) with no evidence of phosphine oxide*** resulting from ligand oxidation. A deliberate attempt to oxidise the complexed ligand under conditions

* This work - Chapter 3, section 3.3.1

** As shown by ^{1}H n.m.r., i.r. and u.v./vis. spectroscopy.

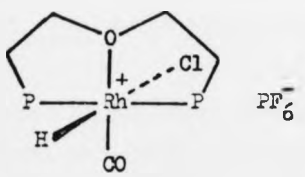
*** ν(P=O) = 1180 (s), 1125 (s) cm^{-1}.

Figure 3.2.5. The Reaction of $RhL_1(Cl)(CO)$ and HCl Gas.

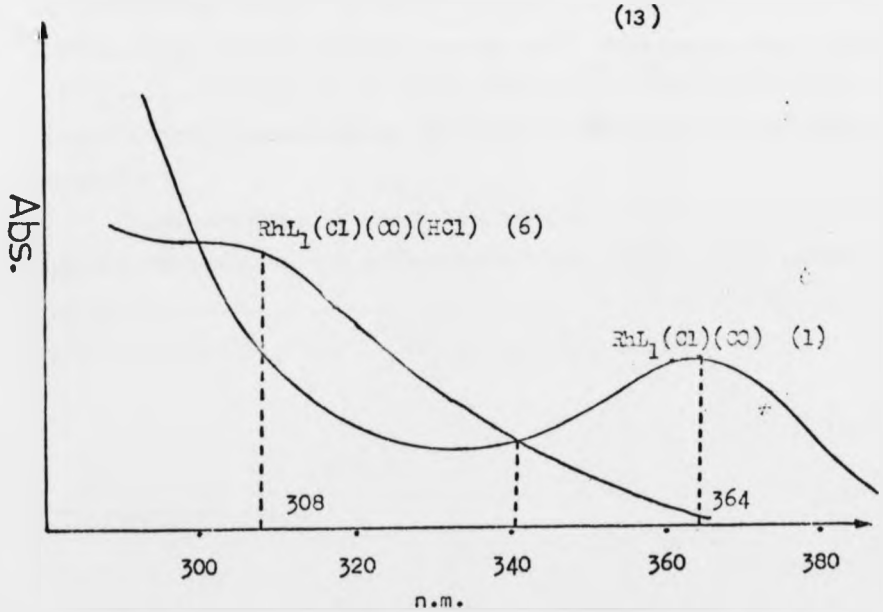


Possible species in solution- no specific cis or trans products are implied.

c.f. the predicted addition product between $(RhL_1CO)^+PF_6^-$ and HCl gas (see section 3.3.1.)



(13)



(excess aqueous H_2O_2 / acetone / CH_2Cl_2) which rapidly oxidise the free ligand, failed, establishing an increased stability on complexation often observed for phosphorus ligands.

3.2.2 The Preparation and Reactions of $RhL_2(Cl)(CO)$ and $RhL_3(Cl)(CO)$

Introduction

The phosphino-ethers L_2 and L_3 are capable of acting as trans bidentate ligands forming 11 and 14 membered chelate rings respectively. As discussed in section 3.1, some controversy exists as to the stability of medium-large chelates of this type. In the previous section the preparation of $RhL_1(Cl)(CO)$, (1), was described; here the analogous complexes (7 and 8) with L_n (n = 2 and 3 respectively) are discussed. To an extent, identification of (7) and (8) is simpler, since the increased chain length reduces the probability of cis isomers. Furthermore, crystal data available* on cationic derivatives of (1), (7) and (8), of the type $[RhL_nCO]^+ PF_6^-$ suggest that M . . . O interactions will be less important in complexes of L_2 and L_3.

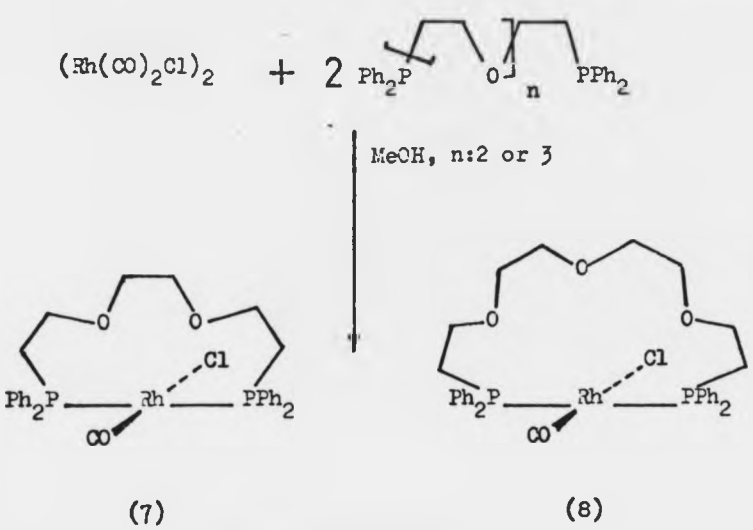
The reactions of L_2 and L_3 with $[Rh(CO)_2Cl]_2$ in MeOH proceeded smoothly as described for L_1, giving yellow microcrystalline products $RhL_n(Cl)(CO)$ (compounds 7 and 8 for L_2 and L_3 respectively). These have very similar chemical and physical properties to (1) and are assigned trans square planar geometries, figure 3.2.6.

I.r. spectra for the series (1), (7) and (8) are almost identical, showing only an increase in intensity and broadening of the ν(C-O-C) band at 1100 cm^{-1}, with increasing chain length. Similarly, the chemical shift equivalence of the protons at C(2) and C(2)' in each structure down to -80°, their progression, namely (1) 4.17 p.p.m., (7) 4.01 p.p.m. and (8) 3.91 p.p.m., and also the lack of coupling, is consistent with an increasing separation of the ligand chain and metal atom, figure 3.2.7.

Those reactions previously described for (1) are observed for (7) and (8) with few differences in reactivity attributable to either O-donor interactions or varying degrees of steric hindrance. Values of K for the reaction of (1), (7) and (8) with dry HCl gas in CH_2Cl_2 give quantitative proof of this. It is thought

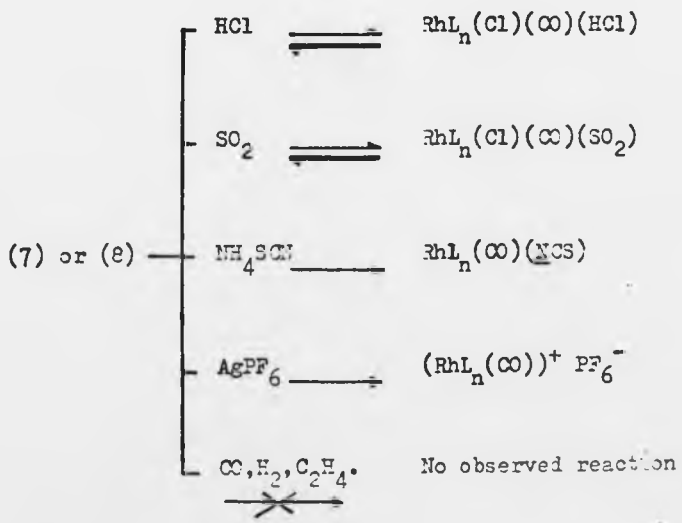
* This work, Chapter 4

Figure 3.2.6. The Reactions of L_n (n:2,3) with $(Rh(CO)_2Cl)_2$



(7) (8)

Yellow Precipitates



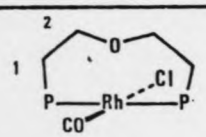
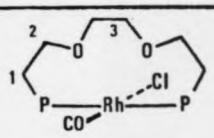
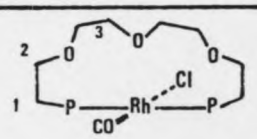
$$RhL_n(Cl)(CO) \xrightarrow[HCl]{K} RhL_n(Cl)(CO)(HCl)$$

Ligand	Compound	K
L_1	(1)	14.4
L_2	(7)	28.6
L_3	(8)	~ 30 *

the observed progression (although hardly significant) probably reflects a slight decrease in steric hindrance with increasing chain length.

* A very approximate estimate obtained by i.r. spectroscopy and included for comparison only.

FIGURE 3.2.7

Property	 (1)	 (7)	 (8)
^{1}H n.m.r. ($CDCl_3$) T.M.S. = 0 p.p.m. all peaks broad	1. 2.90 (s, 4H), 2. 4.17 (s, 4H)	1. 3.04 (s, 4H), 2. 4.01 (s, 4H) 3. 3.36 (s, 4H)	1. 3.05 (s, 4H), 2. 3.91 (s, 4H) 3. 3.36 (s, 8H)
^{31}P n.m.r.	Doublet J (Rh - P_t) = 125.0 c/s**	Doublet J (Rh - P_t) = 128 c/s	Doublet J (Rh - P_t) = 128 c/s
I.r. (Nujol) Values of (CO) in CH_2Cl_2 were ca. 1975 cm^{-1}	ν(CO) = 1965 (s) cm^{-1}	1965 (s)	1965 (s)
	ν(Rh - Cl)* = 300 (m) cm^{-1}	300 (m)	300 (m)
	ν(C - O - C) = 1100 (m) cm^{-1}	1100 (m)	1100 (m)
Analysis :			
For C, H, Cl, O, P, Rh	$C_{29}H_{28}Cl_1O_2P_2Rh_1$	$C_{31}H_{32}Cl_1O_3P_2Rh_1$	$C_{33}H_{36}Cl_1O_4P_2Rh_1$
Calculated	C, 57.19; H, 4.60; O, 5.26; P, 10.19	C, 57.01; H, 4.90; O, 7.36; P, 9.50	C, 56.86; H, 5.17; Cl, 5.10; O, 9.19; P, 8.90
Found	C, 57.21; H, 4.35; O, -- ; P, 10.51	C, 56.9; H, 4.81; O, -- ; P, 9.67	C, 56.95; H, 5.49; Cl, 6.88; O, 7.71; P, 11.98

* A very tentative assignment, since bridging chlorides also have i.r. bands in this region.

**A subsequent spectrum gave: δ(P) = 20.79 p.p.m.(d, J(Rh-P_t) = 125.7 c/s), reference capillary $\delta(H_3PO_4)$ = 0 p.p.m.

SECTION 3.3

Preparation and Properties of Cationic Carbonyl Complexes

Introduction

Square planar d^8 complexes of group VIII b metals show a marked preference for soft donors and complexes involving hard donors such as ether O are comparatively rare. One method for encouraging hard donor bond formation might be the preparation of cationic metal complexes which should have increased hard acid character due to the contraction of the metal orbitals. Some support for this belief is given by the work of Osborn et al.[34] which shows that comparatively stable cationic solvates of the type $[Rh(CO)(\underset{\sim}{L}_2)(S)]^+$, (where S = dmf, acetone, acetonitrile, dimethyl acetamide and $\underset{\sim}{L}$ = PPh_3), may be readily prepared in solution and isolated under suitable conditions. These complexes have formal bonds from comparatively hard nitrogen or ketone donors. It was of considerable interest to investigate the preparation of the analogous cations $[RhL_n(CO)(S)]^+$ from the neutral chlorides (1), (7) and (8). In these systems ligand O-donation might take preference to solvent incorporation.

A number of potential routes exist for generating cationic Rh(I) species from neutral d^8 precursors :

1. The addition of NO^+, PhN_2^+, CH_3CO^+ or H^+ (as their BF_4^- or PF_6^- salts), to complexes of the type $Rh(\underset{\sim}{L})_3Cl$ has been shown to give five coordinate cations[9]

$$Rh(\underset{\sim}{L})_3(Cl) + AX \rightarrow [Rh(\underset{\sim}{L})_3(Cl)(A)]^+ X^-$$

where $\underset{\sim}{L}$ = Ph_3P or the tridentate ligand $(\underset{\sim}{L})_3$ = $PhP(CH_2CH_2CH_2PPh_2)_2$ and A = NO^+, PhN_2^+, CH_3CO^+ or H^+.

This may be viewed as an oxidative addition or, more appropriately, as a Lewis acid association[50] of an electrophile with the Lewis base $Rh(\underset{\sim}{L})_3Cl$. The success of this method is likely to depend upon the Lewis basicity of the metal.

2. More generally, four coordinate Rh(I) cations may be prepared by displacement of chloride anion from a neutral d^8 chloro precursor. Two main routes exist :

2(a). Powerful coordinating bidentate phosphine nucleophiles such as dPe displace chloride anion for $RhCl(Ph_3P)_3$ or $RhCl_3 \cdot 3H_2O$, under mild conditions, reducing the starting material to square planar cations of the type $[Rh(dPe)_2]^+ Cl^-$.[37] More generally, it has been shown that a chelating phosphine is not essential and an extensive survey by Osborn et al[34] demonstrates that cationic complexes may be prepared in a variety of polar media using Ph_3P as nucleophile.

$$[Rh(diene)Cl]_2 \underset{-L}{\overset{+L}{\rightleftharpoons}} RhCl(diene)\underset{\sim}{L} \underset{-L}{\overset{+L}{\rightleftharpoons}} [Rh(diene)\underset{\sim}{L}_2]^+ Cl^-$$

$$\downarrow H_2/\text{solvent}$$

$$[Rh(diene^*)\underset{\sim}{L}_2]^+ \xleftarrow[\text{diene}^*]{\text{excess}} [RhH_2\underset{\sim}{L}_2S]^+$$

$$\downarrow CO$$

$$[Rh(CO)(\underset{\sim}{L}_3)]^+ \xleftarrow{\underset{\sim}{L}} [Rh(CO)(\underset{\sim}{L}_2)(S)]^+$$

$\underset{\sim}{L} = Ph_3P$

(diene) is typically bicyclo[2.2.1] hexadiene

(diene*) is typically 1,5-C_8H_{12}, 1,3-butadiene, cyclopentadiene, cyclo-1,3-hexadiene.

2(b). The Rh-Cl bond is readily cleaved by metal salts of large and stable anions ; for example, the Ag, Na and K salts of perchlorates, tetraphenylborates, tetrafluoroborates and hexafluorophosphates. When this reaction is carried out in the presence of alternative nucleophiles, stable cationic species may be isolated[34, 9] e.g.

$$Rh(Cl)(\underset{\sim}{L})_3 + AgPF_6 + \text{diene} \rightarrow [Rh(\text{diene})(\underset{\sim}{L}_2)]^+$$

$$Rh(Cl)(L^*) + AgPF_6 + CO \rightarrow [RhL^*CO]^+$$

where $\underset{\sim}{L} = Ph_3P$ and $L^* = PhP(CH_2CH_2CH_2PPh_2)_2$.

The use of salts of stable anions represented the most facile route for producing cationic derivatives of $RhL_n(Cl)(CO)$ where n = 1, 2 and 3, with the added advantage that the reaction may be carried out in a non-coordinating solvent such

as CH_2Cl_2, precluding competing ligand donation from the solvent.

3.3.1 The Preparation and Reactions of $[RhL_1(CO)]^+$

$RhL_1(Cl)(CO)$, (1) reacts instantly with an equimolar quantity of silver hexafluorophosphate in CH_2Cl_2 (or silver tetrafluoroborate), followed by recrystallisation from MeOH, to give beautiful bright yellow crystals of the monomeric salt $[RhL_1CO]^+ PF_6^-$ (9). (9) is neither air nor moisture sensitive and whilst apparently indefinitely stable at 20^o, rapidly decomposes above 50^o, giving unidentifiable products. The structure has been completely determined by single crystal X-ray methods* and is shown schematically in figure 3.3.1. The single, most significant, feature of this complex is the occupation of the fourth coordination site at the metal by the chain O-donor of L_1. (9) has one of the largest in plane distortions from square planarity ever observed for a Rh(I) complex with P - Rh - P = 166^o.** Conductivity is typical of a 1 :1 electrolyte (Λ_m = 144.8, acetone, 20^o and 10^{-3} M) and crystal data confirm that there is no significant interaction between anion and cation in the solid state.

Spectral and analytical data for (9) are presented in figure 3.3.2. The ^{31}P spectrum shows the expected doublet with J(Rh - P_t) = 129.0 c/s ; this is similar to that observed in the neutral precursor (1), where J(Rh - P_t) = 125.0 c/s, and this lends support for the transoid structure of (1). The i.r. spectrum (nujol) shows a strong band at 835 cm^{-1}, characteristic of the PF_6^- counterion and a high field shift for the carbonyl frequency, [ν(CO) = 2005 cm^{-1}] relative to (1), [ν(CO) = 1965 cm^{-1}, nujol] which it resembles in all other respects. ^1H n.m.r. (acetone) shows the expected peaks corresponding to the methylene protons at C(1) and C(2). 3.21 (broad multiplet, 4H at C(1)) and 4.42 (septuplet, 4H at C(2)) respectively and aromatic peaks at ca. 7.7 (broad, 8H, ortho) and 7.36 (broad, 12H, meta and para). Crystal data show that hybridisation at oxygen is close to sp^3, with O(1) - C(2) and O(1) - C(3) syn to the metal ligand plane. Rapid inversion about oxygen occurs in solution. since axial and equatorial protons at C(2) are equivalent in the ^1H n.m.r. spectrum down to -80^o.

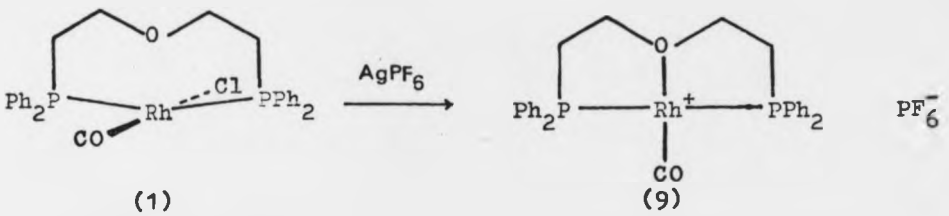
The Rh - O Bond

The preparation and characterisation of (9) establishes that the phosphinoether L_1 is both geometrically and electronically capable of functioning as a tridentate chelating ligand. It is of interest to compare the chemistry of (9) with that of the solvates $[Rh(CO)(Ph_3P)_2(S)]^+$ to establish the relative importance of chelation in stablising the Rh - O bond.

* This work. Chapter 4, section 4.2.

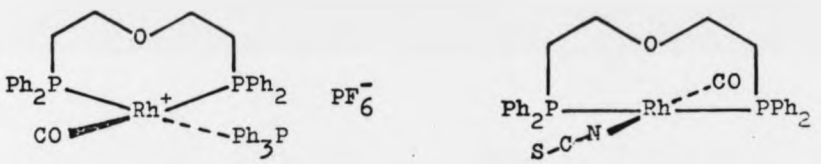
** Ref. J. J. Geary, Coord.Chem.Reviews, 1971, 7, 91.

Figure 3.3.1. The Preparation and Reactions of $(RhL_1CO)^+ PF_6^-$.

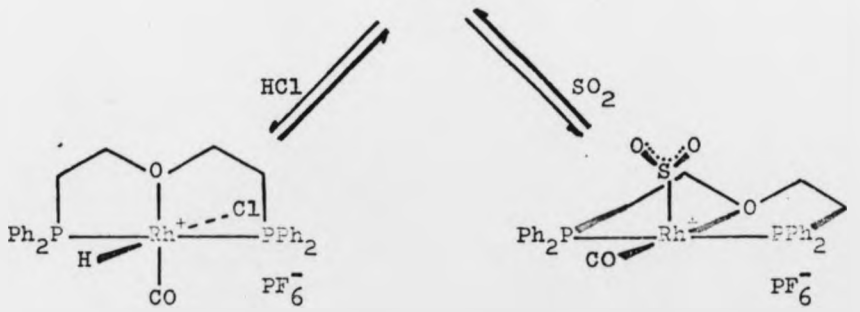


(1)
Yellow microcrystals

(9)
Yellow crystals from MeOH

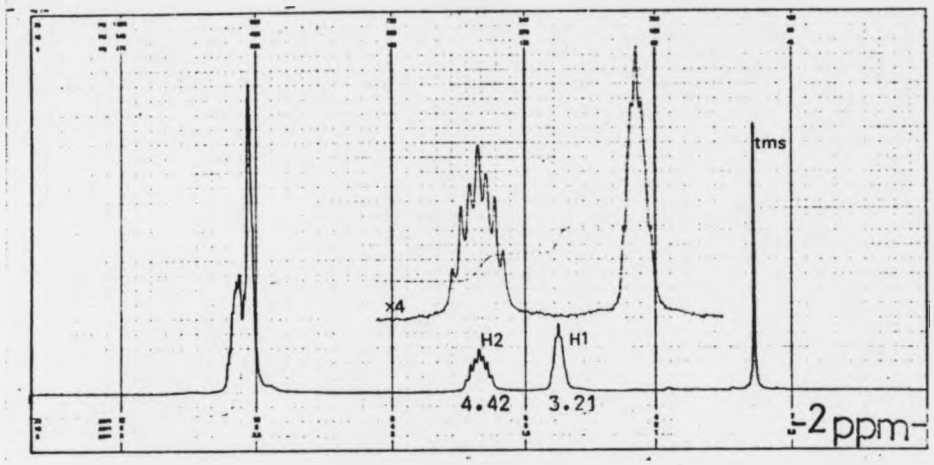


(11) (4)

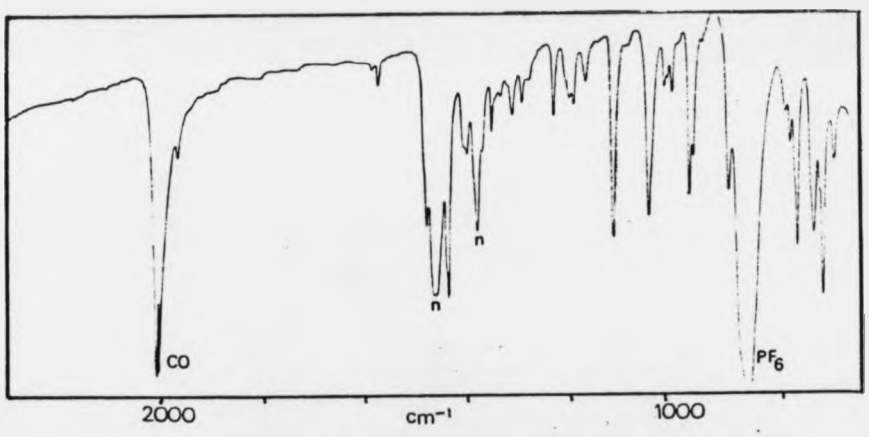


(13) (12)

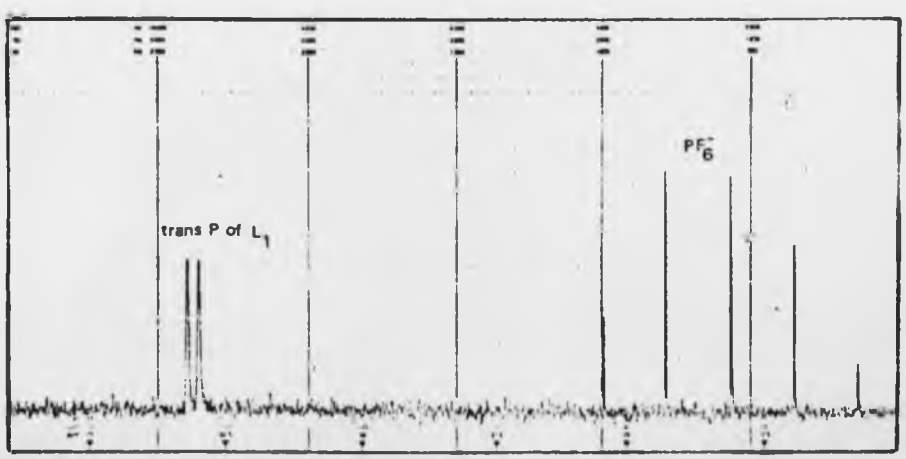
Figure 3.3.2. Spectral Data for $(RhL_4CO)^+ PF_6^-$



^1H n.m.r. of (9) ($CDCl_3$), 300°K, reference t.m.s.=0 p.p.m.
(1 large scale division= 2 p.p.m.)



I.r.(Nujol mull) of (9).



^{31}P spectrum of (9).

Osborn did not report[34] synthesis of $[Rh(CO)(Ph_3P)_2(Me_2\underline{O})]^+$ (10) which both electronically and sterically would be a good non-chelated analogue of (9). We attempted to synthesise (10) from $Rh(Cl)(CO)(Ph_3P)_2$ by a route closely similar to that used for (9).

$$Rh(Cl)(CO)(Ph_3P)_2 + AgPF_6 \xrightarrow[-80^\circ]{} [Rh(CO)(Ph_3P)_2(S)]^+$$

(10)

$+ Me_2O$

yellow solution at -80°

↓

Decomposition at 20°

A solution of $Rh(Cl)(CO)(Ph_3P)_2$ and $AgPF_6$ in Me_2O at -80° was bright yellow and AgCl was quantitatively precipitated. On warming to 20° the solution rapidly became dark brown and removal of solvent in vacuo gave a brown solid with properties not consonant with the expected dimethyl etherate (10). Failure to produce (10) indicates that chelation may well stabilise the Rh - O bond in (9).

In the preparation of (9) care was taken to avoid the use of solvents such as acetone, CH_3CN or Et_2O which might have competed with the ligand chain O-donor. This proved to be unnecessary since repetition of the reaction using solvent mixtures of CH_2Cl_2 :S (50 :50) [where S = acetone, acetonitrile or dmf] did not alter the course of reaction. (9) might therefore be considered as an internally solvated cation similar to the known[34] cations $[Rh(CO)(Ph_3P)_2(S)]^+$ but having added stability due to chelation.

Osborn reported[34] that solvent is readily displaced from $[Rh(CO)(Ph_3P)_2S]^+$ by Ph_3P, giving $[Rh(CO)(Ph_3P)_3]^+$. Similarly, we find that an equimolar mixture of Ph_3P and (9) in Et_2O gives $[RhL_1(CO)(Ph_3P)]^+ PF_6^-$ (11). (11) was obtained as a crystalline yellow solid from MeOH having an i.r. spectrum (nujol) almost identical to (9), apart from $\nu(CO) = 1995\ cm^{-1}$ which became broader and weaker. ^1H n.m.r. confirmed that a molecule of Ph_3P had been incorporated and although the chemical shifts of the ligand methylene protons at C(1) and C(2) were virtually unaltered from their values in (9), all fine coupling was lost. Accordingly, (11) is assigned the structure shown (figure 3.3.1) without ligand O donating to the metal. Treatment of $[Rh(CO)(Ph_3P)_3]^+$ with CO is reported[34] to afford $[Rh(CO)_2(Ph_3P)_3]^+$. When a solution of (11) in CH_2Cl_2 was treated with CO at ambient temperature and pressure, no reaction was observed. Failure to produce a CO adduct of (11) reflects the steric hindrance which models show must arise in any five coordinate L_1 analogue of

$[Rh(CO)_2(Ph_3P)_3]$.

The only other reaction observed in which the Rh - O bond is cleaved occurs when (9) is treated with NH_4SCN in MeOH at 20°

$$(9) + NH_4SCN \longrightarrow [Rh L_1 CO(\underline{N}CS)] \ (4) + NH_4PF_6$$

This results in immediate precipitation of the neutral N bonded isothiocyanate (4) which has previously been prepared by the slow exchange reaction between (1) and NH_4SCN (vide supra).

Oxidative Addition Reactions

The oxidative reactivity of (9) is very similar to that observed for the neutral precursor (1). For example, a solution of (9) in CH_2Cl_2 shows no tendency to react with CO, H_2, butadiene or ethylene at ambient temperature and pressure. This contrasts with the behaviour of $[Rh(CO)(Ph_3P)_2(S)]^+ PF_6^-$ which reacts readily with CO and a variety of dienes :

$$[Rh(CO)(Ph_3P)_2(S)]^+ \xrightarrow{CO} [Rh(CO)_3(Ph_3P)_2]^+ \xrightarrow{diene} [Rh(CO)(diene)(Ph_3P)_2]^+$$

Reversible reaction does occur with SO_2 and HCl gas in CH_2Cl_2. A solution of (9) saturated with SO_2 at 20° showed new i.r. bands attributable to an SO_2 adduct (12), which disappeared on bubbling dry N_2 through the solution.

$$(9) + SO_2 \longrightarrow [Rh L_1(CO)(SO_2)]^+ PF_6^-$$

(12)

$\nu(SO_2)$ = 1220, 1195, 1060 cm^{-1}

$\nu(CO)$ = 2040 cm^{-1}

The species in solution may well arise from addition of SO_2 to the square planar cation without ligand O displacement. The predicted geometry is tetragonal pyramidal with SO_2 at the apex and trans L_1 and CO forming the base as is observed in the complexes $[Ir(CO)Cl(PPh_3)_2(SO_2)]$ M = Rh, Ir.[47,48] The equilibrium const. for the reaction is such that no solid adduct could be isolated.

Similarly, passage of dry HCl gas through a CH_2Cl_2 solution of (9) gave infrared evidence of the reversible formation of an HCl adduct (13). Again,

$$(9) + HCL \longrightarrow [Rh L_1(CO)(HCl)]^+ PF_6^-$$

(13)

ν(Rh - H) = 2100 cm^{-1}

ν(Rh - CO) = 2080 cm^{-1}

no solid adduct could be isolated and on the basis of the limited data available, the structure shown (figure 3.3.1) may represent a possible species in solution, although no specific prediction on whether HCl adds cis or trans can be made.

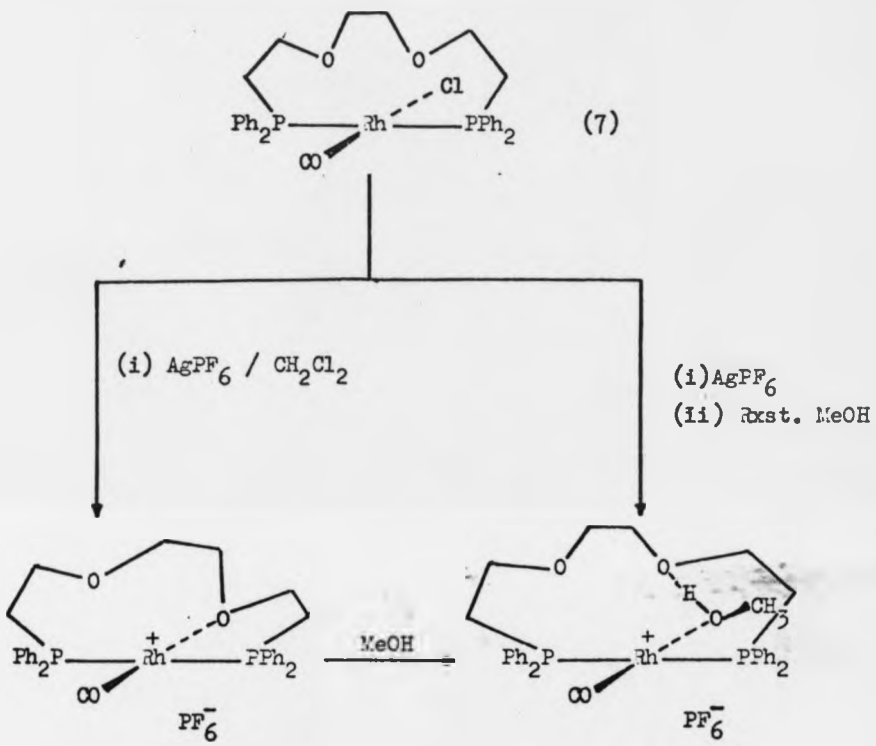
3.3.2 The Preparation and Reactions of $[Rh(L_2)(CO)(MeOH)]^+ PF_6^-$

Treatment of $RhL_2(Cl)(CO)$, (7) with an equimolar quantity of $AgPF_6$ in CH_2Cl_2 (20^o), followed by filtration and removal of solvent in vacuo, gave a yellow microcrystalline powder, $[RhL_2CO]^+ PF_6^-$ (14). This showed no evidence of incorporated solvent molecules as shown by i.r. (nujol/H.C.B) and ^1H n.m.r. ($CDCl_3$). Accordingly, it is believed that (14) is an O-bonded analogue of (9) which might have a structure similar to that shown (figure 3.3.3). Recrystallisation of (14) from MeOH affords large bright yellow prisms of an MeOH solvate $[Rh(L_2)(CO)(MeOH)]^+ PF_6^-$ (15). This is an interesting process. When (14) is added to MeOH at 20^o (ca. 0.4 g in 2 ml MeOH) it dissolves instantly with no noticeable temperature change, affording a clear yellow solution. After from 1 to 10 minutes, almost 90% of the material is suddenly deposited as beautiful yellow prisms, the solubility of the solvate (15) thus produced being markedly lower than that of (14). The structure of (15) has been partially determined by X-ray crystallography* - at the current level of refinement (R = 0.75) the gross structure is as shown (figure 3.3.3). The coordination about rhodium is confirmed to be distorted trans square planar with L_2 acting as a trans bidentate P-donor and an MeOH molecule occupying the fourth coordination site at the metal. It is possible that the MeOH molecule is hydrogen bonded to an O-donor in the ligand chain and this would help to explain the rather specific solvation properties observed. I.r. (nujol/H.C.B) and ^1H n.m.r. (d^6 acetone) confirms the presence of one mole of MeOH per mole of complex, with ν(OH) = 3250 cm^{-1} (very broad and weak) and δ (MeOH) = 3·37 and δ(MeOH) = -** p.p.m. respectively. Binding of MeOH is not strong, since several cycles of dissolution in acetone followed by removal of solvent in vacuo displaces it from the complex. The driving force for solvent incorporation must derive from non-bonded H-H interactions in the ligand chain; which models confirm will arise in any terdentate analogue of (7). The solvent specificity observed is attributed to hydrogen bonding requirements of the solvent donor and ligand chain and this will be clarified when accurate crystal data become available.

Spectral and analytical data are presented in figures 3.3.4 and 3.3.5. The i.r. spectrum of (15) (nujol) closely resembles that of the non-solvated cation (7), except that the carbonyl frequency (ν(CO) = 1980 cm^{-1}) is 25 cm^{-1} to lower frequency. ^1H n.m.r. is analogous to that observed for (7); in particular the

* This work, Chapter 4
** Not observed

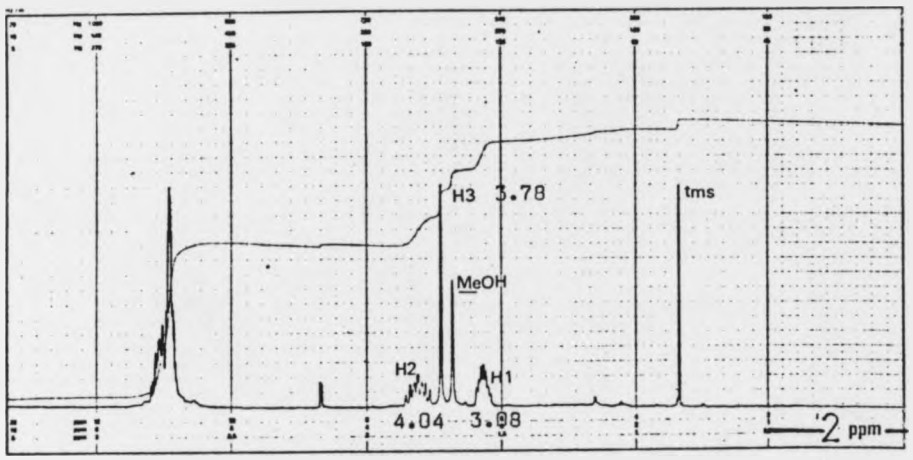
Figure 3.3.3. The preparation and Reactions of $(RhL_2CO)^+ PF_6^-$ and $(RhL_2CO(MeOH))^+ PF_6^-$



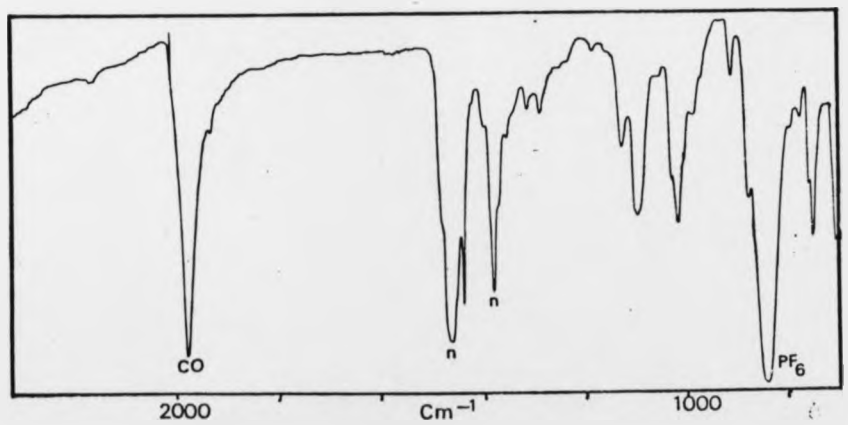
(14) (15)

Yellow solid Yellow crystals

Figure 3.3.5. A. Spectral Data for $(RhL_2CO(MeOH))^+ PF_6^-$, (15).



^1H n.m.r. of (15) in CD_2Cl_2 at 303°K, t.m.s.= 0p.p.m., 1 large scale division= 2p.p.m. .



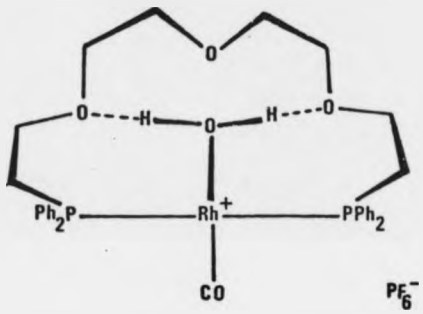
I.r. spectrum (nujol mull) of (15), nujol peaks='n'.

chemical shift equivalence of the protons at C(2) and C(2)$^{-}$, down to -80^{o} (4.04 p.p m), is consistent with the proposed structure if rapid interconversion of O-bonded tautomers occurs.

The chemistry of (15) is unremarkable and compares closely with $[RhL_1(CO)]^{+}PF_6^{-}$ (9). For example, (15) reacts with NH_4SCN to give a neutral N-bonded isothiocyanate, $Rh(L_2)(CO)(NCS)$ (16) and with Ph_3P to give $[Rh(L_2)(CO)(Ph_3P)]^{+}PF_6^{-}$ (17). Furthermore, reversible reaction appears to occur with dry HCl or SO_2 gas in CH_2Cl_2 at ambient temperature and pressure. Despite the fact that (15) ostensibly resembles the known solvates $[Rh(CO)(Ph_3P)_2(S)]^{+}$, its reactivity towards CO and diene substrates is greatly reduced since no labile ligand is available for replacement. As observed with (9), CH_2Cl_2 solutions of (15) show no tendency to react with CO or butadiene at ambient temperatures and pressures. It is probable that this low reactivity is attributable in part to steric hindrance from the ligand chain.

3.3.3 The Preparation of $[Rh(L_3)(CO)(H_2O)]^+ PF_6^-$

The reaction of equimolar quantities of $Rh(L_3)(Cl)(CO)$ (8) and $AgPF_6$ in CH_2Cl_2 proceeded smoothly as previously described in the preparation of (9) and (15). Recrystallisation from MeOH gave yellow prisms of $[Rh(L_3)(CO)(H_2O)]^+ PF_6^-$ (18). Single crystal X-ray data for (18)* shows a trans square planar geometry at the metal with L_3 acting as a trans bidentate P-donor. The fourth coordination site at the metal is occupied by a water molecule which is hydrogen bonded at two points to the ligand chain as shown schematically below.

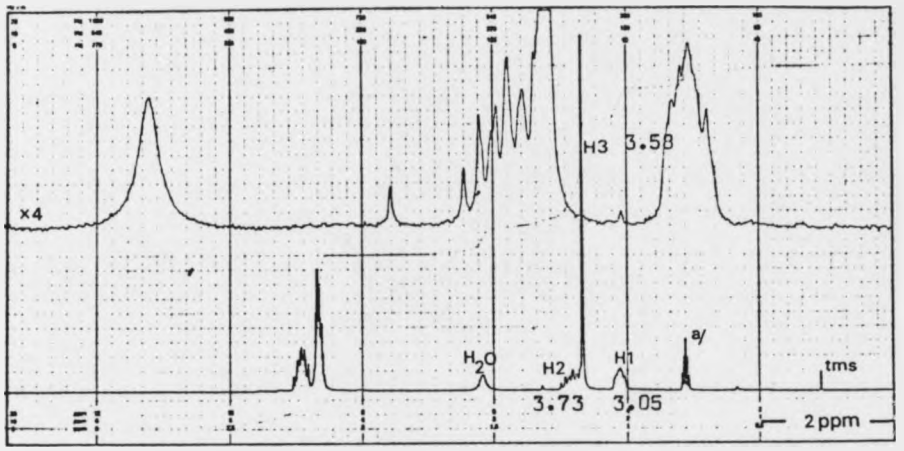


(18)

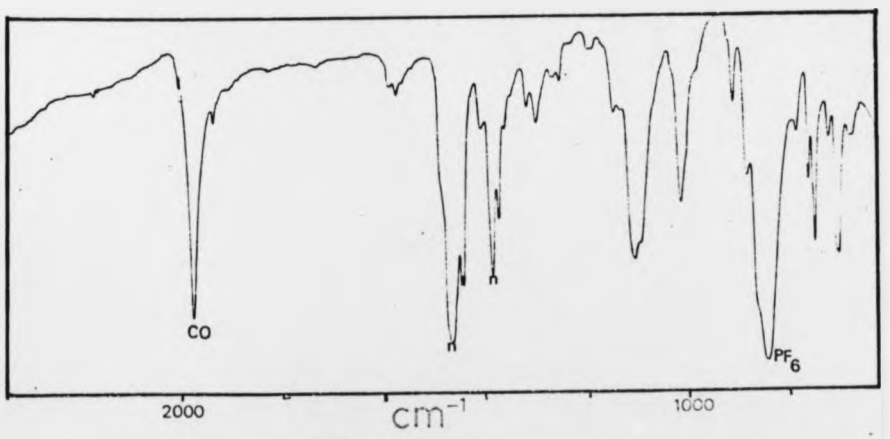
^1H n.m.r. confirms the presence of one molecule of H_2O per molecule of complex, $\delta(H_2O) = 6.04$ p.p.m., and also indicates that binding is strong since several cycles of dissolution in carefully dried acetone and removal of acetone in vacuo, followed by a repetition of this procedure with chloroform, produced no change in either the proton integral or the chemical shift of the bound H_2O molecule. However, either rapid exchange of the H_2O protons or, less likely, rapid exchange of the entire H_2O molecule must occur in wet acetone, since addition of D_2O to an acetone solution of (18) caused immediate collapse of the bound H_2O signal. Again, the solvation properties of (18) are highly specific. (18) was recovered unchanged after recrystallisation from a carefully dried MeOH/EtOH/Et_2O solvent mixture. Furthermore all attempts to prepare an unsolvated species failed and H_2O incorporation appeared to take place during the initial reaction of (8) with $AgPF_6$ in CH_2Cl_2. ^1H n.m.r. confirmed that (8) was ostensibly dry and i.r. spectroscopy showed no trace of H_2O in the CH_2Cl_2 solvent. It was concluded that H_2O had been introduced with the $AgPF_6$ which is known to be extremely hygroscopic, and from which the last traces of H_2O are removed only with great difficulty. It therefore appears unlikely that

* This work, Chapter 4.

Figure 3.3.5. B. Spectral Data for $(RhL_3CO(H_2O))^+ PF_6^-$, (18).



^1H n.m.r. spectrum of (18) in d^6 acetone at 300°K, t.m.s.= 0p.p.m. 1 large scale division= 2p.p.m., peak 'a' is d^6 acetone.



I.r. spectrum (nujol mull) of (18), nujol peaks='n'.

(18) can be prepared as an MeOH solvate analogous to (14) by the exclusion of H_2O and subsequent introduction of MeOH. Models clearly indicate that the driving force for solvent incorporation derives from the severe non-bonded H - H interactions which arise in any attempt to force L_3 to function as a terdentate donor. Crystal structure data show that the specificity for H_2O is a result of a fortuitous arrangement of chain O-donors with respect to the metal atom. This creates a cavity into which an H_2O molecule fits exactly, whilst being stabilised both by O-donation to the metal and hydrogen bonding of both protons to O-donors of the ligand chain. Furthermore, with the ligand chain in this conformation, non-bonded H - H interactions are minimised.

Spectral and analytical data for (18) are presented in figures 3.3.4 and 3.3.5. The i.r. spectrum (nujol) is virtually identical to that of the L_2 adduct (15). The ^{1}H n.m.r. (d^6 acetone) is also completely comparable with the spectrum observed for (15). As expected, the chemical shifts of the protons at C(2) and $C(2)^-$ are equivalent down to - 80° and this supports the belief that the gross solid state structure is maintained in solution. A comparison of the ^{1}H n.m.r. spectra for the series of cations, namely (9), (15) and (18) (figure 3.3.4), shows :

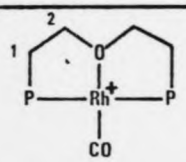
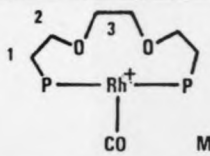
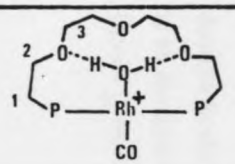
(i) A small progressive upfield shift for the protons at C(1) and $C(1)^-$: (9) = 3.21 ; (15) = 3.08 and (18) = 3.05 p.p.m. respectively.

(ii) A much larger shift in the same sense for the protons at C(2) and $C(2)^-$: (9) = 4.42 ; (15) = 4.04 and (18) = 3.73 p.p.m. respectively.

(iii) Small but significant decreases in the two and three bond phosphorus couplings to the protons at C(1) and C(2) respectively with no change in the proton-proton coupling constant $J(H_1 - H_2)$ = 5.5 c/s.

It is thought that the progressive upfield shift for the protons at C(2) and $C(2)^-$, which tends towards the value of ca. 3.5 p.p.m. observed in free L_n, reflects an increasing separation of the ligand chain from the metal, with a concomitant reduction in direct rhodium - ligand O interaction. Some support for this belief is given by the crystal structures of (9), (15) and (18) which show this to be the case in the solid state. Although it is not easy to assess how the different solvent

FIGURE 3.3.4

Property	 (9)	 (15) MeOH	 (18)
^{1}H n.m.r. (d^6 acetone) T.M.S. = 0 p.p.m.	1. 3.21 (m, 4H), 2. 4.42 (m, 4H) J(1-2) = 6.0 J(P-1) = 3.5, J(P-2) = 11.5 c/s	1. 3.08 (m, 4H), 2. 4.04 (m, 4H), 3. 3.78 (s, 4H). J(1-2) = 5.5, J(P-1) = 3.0, J(P-2) = 10.5 c/s	1. 3.05 (m, 4H), 2. 3.73 (m, 4H), 3. 3.58 (s, 8H). J(1-2) = 5.5, J(P-1) = 2.0, J(P-2) = 9.5 c/s
^{31}P n.m.r.	Doublet J(Rh-P$_t$) = 129 c/s *	Doublet J(Rh-P$_t$) = 129 c/s	Doublet J(Rh-P$_t$) = 129 c/s
I.r. (Nujol/ H.C.B)	ν(CO) = 2005 cm^{-1} (s)	ν(CO) = 1980 cm^{-1} (s) ν(CH_3OH) = 3250 cm^{-1} (broad, weak)	ν(CO) = 1980 cm^{-1} (s) ν(H_2O) = 3200 cm^{-1} (broad, v.weak)
Analysis :			
For C, H, F, O, P, Rh	$C_{29}H_{28}F_6O_2P_3Rh_1$	$C_{32}H_{36}F_6O_4P_3Rh_1$	$C_{33}H_{38}F_6O_5P_3Rh_1$
Calculated	C, 48.47; H, 3.90; O, 4.46; P, 12.95; Rh, 14.35	C, 48.36; H, 4.53; O, 8.06; P, 11.71; Rh, 12.97	C, 48.06; H, 4.61; P, 11.29 Rh, 12.50
Found	C, 48.42; H, 3.99; O, 6.51 P, 16.92; Rh, 13.60	C, 48.30; H, 4.28; P, 12.48; Rh*, 20.46 * rhodium oxyfluorides ?	C, 48.01; H, 4.67; P, 13.16; Rh, 13.54

* δ(P) = 165.63 p.p.m. reference against (PF_6^-) = 0 p.p.m.

donors in these complexes will modify the chemical shift of the protons at C (2), it is thought that a value of ca. 4.4 p.p.m. might be a useful inference of metal - ligand O bonding in cationic complexes of this type.

SECTION 3.4

The Preparation of $Rh\,L_1(Cl)(C_2H_4)$

Introduction

L_n (n = 1 , 2, 3) form well characterised neutral and cationic complexes, $Rh\,L_n(Cl)(CO)$ and $[Rh\,L_n(CO)(S)]^+PF_6^-$ in which the ligands function as bidentate *trans* donors. These complexes are of considerable structural interest; however, the chemistry is unremarkable, in general reflecting that of the known triphenylphosphine analogues, with the additional constraint that steric hindrance from the ligand chain further reduces reactivity.

Treatment of $[Rh\,Cl\,(C_2H_4)_2]_2$ with 2 equivalents of Ph_3P in benzene saturated with ethylene is known to afford the square planar adduct *trans* $Rh\,Cl\,(C_2H_4)(PPh_3)_2$.[5] In solution this rapidly loses ethylene, affording a dimer $[Rh\,(Cl)(PPh_3)_2]_2$. The analogous reaction of $[Rh\,Cl\,(C_2H_4)_2]_2$ with L_1 was expected to yield $Rh\,L_1(Cl)(C_2H_4)$.

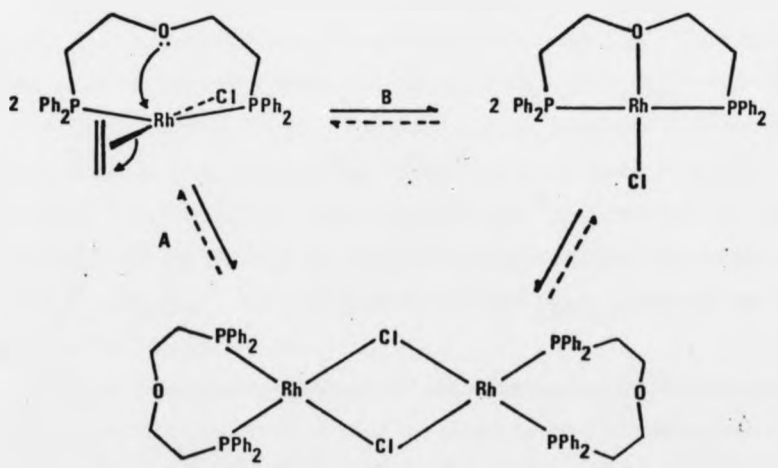


FIGURE 3.4.1.

In this complex very ready loss of ethylene might be promoted by ligand O-donation to the metal. This could merely facilitate formation of the dimer $[RhL_1Cl]_2$ as observed for $RhCl(PPh_3)_2(C_2H_4)$,[5] route A, figure 3.4.1. However, we were interested in the possibility of forming neutral square planar species of the type $RhL_1(Cl)$ with L_1 acting as a tridentate donor as observed in $[RhL_1CO]^+ PF_6^-$, route B.

3.4.1 Reaction of L_1 with $[Rh(C_2H_4)_2Cl]_2$

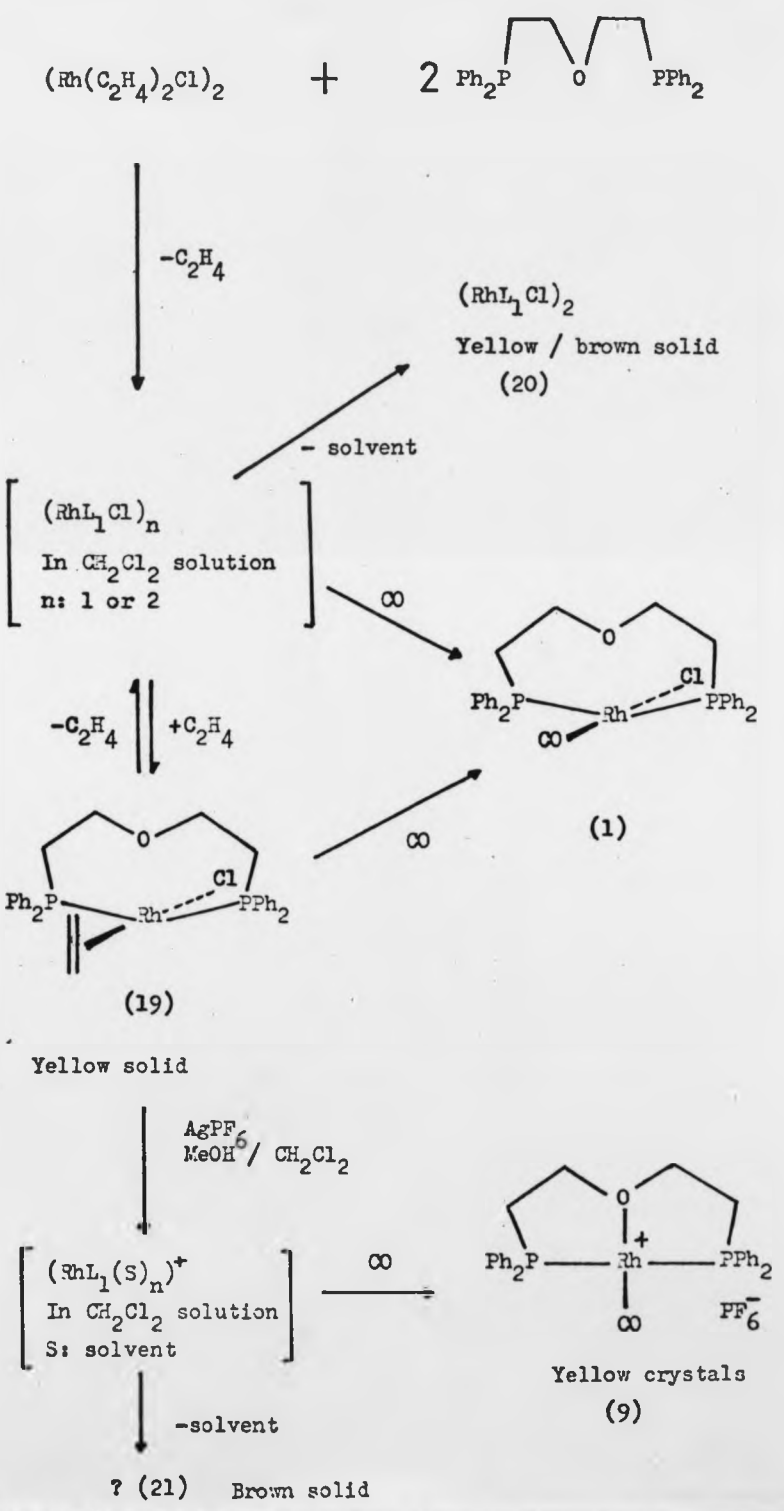
Treatment of a slurry of $[Rh(C_2H_4)_2Cl]_2$ in ethylene saturated MeOH/CH_2Cl_2 with L_1 in ethylene saturated CH_2Cl_2 at 20° (1 :2 molar ratio) afforded a pale yellow/orange solution, believed to be an equilibrium mixture of $RhL_1(Cl)(C_2H_4)$ (19) and $[RhL_1Cl]_n$ (20) species by analogy with the corresponding triphenylphosphine-rhodium system,[5] figure 3.4.2. Reversible loss of a further mole of ethylene occurs readily on passing nitrogen gas through the solution, giving a deep red/brown colour, the original chromophore being very slowly restored on treatment with ethylene. Evaporation of CH_2Cl_2 from the initial CH_2Cl_2/MeOH solution with a stream of ethylene over 3 hours at ca. 10° gave a bright yellow precipitate $RhL_1(Cl)(C_2H_4)$ (19); attempts to precipitate (19) from the CH_2Cl_2 solution by addition of hexane gave mixtures of (19) and (20). (19) loses ethylene slowly in the solid state (ca. 2 hours at 10^{-3} mm Hg) but very rapidly in solution, giving (20) as a yellow/brown solid. Treatment of either (19) or (20) as slurries in MeOH with CO gives $RhL_1(Cl)(CO)$ (1) which has previously been prepared from L_1 and $[Rh(CO)_2Cl]_2$, vide infra.

Physical measurements on solutions of (19), (CH_2Cl_2 or benzene) are complicated since the equilibrium loss of ethylene favours (20). This is completely analogous to the behaviour observed for $RhCl(C_2H_4)(Ph_3P)_2$,[5] and ^1H n.m.r. ($CDCl_3$) shows a broad band at δ 3.5 p.p.m. attributable to ethylene with an integral which reduces on standing. Both ^1H n.m.r. and i.r. (nujol) show the expected L_1 resonances and $\nu(Rh-Cl) = 310\ cm^{-1}$ is assigned to* chlorine trans to ethylene. On the basis of the close similarity of (19) to the known complex trans $RhCl(C_2H_4)(Ph_3P)_2$,[5] it is assigned a distorted trans square planar structure as postulated for $RhL_1(Cl)(CO)$.

There is no strong evidence for the existence of stable monomeric species of the type RhL_1Cl in solution. Whilst the facile loss of ethylene from (19) might imply Rh-O interactions, this could easily be just a steric effect. Although no molecular weight data is yet available for solid $[RhL_1Cl]_n$ (20), it is believed to be the chloro-bridged dimer shown. This is supported by the formation of a monomeric CO derivative and the high solubility of (20) in CH_2Cl_2, $CHCl_3$ or benzene. ^1H n.m.r. and i.r. spectra are in agreement with this, showing the expected L_1 bands and no evidence of incorporated ethylene. In addition an i.r. band at $300cm^{-1}$ is probably* attributable to Cl bridge bonds (cf. $[RhCl(Ph_3P)_2]_2$, $\nu(Rh-Cl) = 303\ cm^{-1}$.[40]

*Both terminal and bridging Rh-Cl bands lie at ca 300-310 cm^{-1} in complexes of this type. With limited data the mode of bonding cannot be specified.

Figure 3.4.2. The Preparation and Reactions of $RhL_1(Cl)(C_2H_4)$



Attempted Preparation of Cationic Derivatives of $RhL_1(Cl)(C_2H_4)$

Treatment of an equilibrium mixture of (19) and (20) under ethylene in CH_2Cl_2/MeOH with $AgPF_6$ gave an immediate precipitate of AgCl and caused the pale yellow/orange solution to become deep red/brown. Removal of solvent in vacuo gave a brown cationic solid (21), ($\nu(PF_6^-) = 830\ cm^{-1}$) which was not the desired $[RhL_1(C_2H_4)]^+ PF_6^-$, figure 3.4.2. Both ^1H n.m.r. and i.r. showed the presence of L_1 but there was no evidence of ethylene. (21) would not recrystallise readily and analytical results for a series of such reactions were variable and inconsistent with chemically reasonable structures. Whilst the nature of isolated (21) is unknown, the freshly prepared solution may contain cationic solvates of the type $[RhL_1(S)_n]^+ PF_6^-$ (where S = MeOH or CH_2Cl_2), since it is possible to isolate $[RhL_1CO]^+ PF_6^-$ (9) in good yield by passing CO through the solution for several minutes. (9) has previously been prepared from $RhL_1(Cl)(CO)$ and $AgPF_6$, vide supra.

3.4.2 The Reactions of L_n (n = 2, 3) with $[Rh(C_2H_4)_2Cl]_2$

Treatment of an MeOH/CH_2Cl_2 slurry of $[Rh(C_2H_4)_2Cl]_2$ under ethylene, with two moles of L_n (for n = 2 or 3) afforded a red/brown precipitate which was only slightly soluble in CH_2Cl_2, similar results being obtained with benzene as solvent. I.r. (nujol) showed the expected L_n absorptions but ν(Rh-Cl) = 310, 285 (br), 250 cm^{-1} was indicative of both monomeric and dimeric chloro-bridged species. Separation of discrete monomeric or dimeric L_n (n = 2, 3) analogues of $RhL_1(Cl)(C_2H_4)$ or $[RhL_1Cl]_2$ has not been achieved. Similarly, treatment of the above product mixtures with CO afforded yellow/brown solids which, although showing evidence of CO (ν(CO) = 1975, broad, nujol), had low solubilities in CH_2Cl_2 and contained little, if any, monomeric $RhL_n(Cl)(CO)$.

Failure to produce L_n (n = 2 or 3) analogues of $RhL_1(Cl)(C_2H_4)$ and $[RhL_1Cl]_2$ is surprising, especially in view of the ready preparation of the series $RhL_n(Cl)(CO)$ (n = 1, 2 or 3) in which there appears to be no differentiation between L_n of increasing chain length. This behaviour is probably closely related to both the increased lability of ethylene in these complexes as compared with CO in $RhL_n(Cl)(CO)$ and also to the tendency to form dimeric chloro-bridged species.

SECTION 3.5

Iridium Complexes of Phosphino-ethers : $IrL_2(Cl)(CO)$ and $IrL_1(Cl)(C_2H_4)$

Introduction

In an attempt to prepare iridium analogues of the phosphino-ether rhodium complexes already discussed, three potentially useful synthetic routes have been investigated :

A. The reaction of L_n with the solution obtained by passing CO through a refluxed solution of chloroiridic acid in alcohols (ethanol, methanol or ethoxyethanol).[19, 51, 52, 56]

B. The reaction of L_n with $IrCl_3$ in dimethylformamide, as in the preparation of Vaska's compound.

C. The reaction of L_n with $[(C_2H_4)_2IrCl]_2$[31, 57 - 58] which follows the method of alkene replacement generally applied in the synthesis of Rh(I) compounds.[53 - 55]

Methods A and C have shown some evidence of success.

3.5.1 Method A : The Complexes $(IrHCl_2(CO)L_2)$ and trans $IrCl(CO)(L_2)$

Shaw et al. have reported fair yields of complexes trans $(IrCl(CO)(R_3P)_2)$ and $(IrHCl_2(CO)(R_3P)_2)$ when two molar equivalents of a phosphine are added to a solution obtained by bubbling CO through chloroiridic acid refluxed in alcohols (EtOH or ethoxyethanol).[51, 52, 56] This reaction has also been postulated to afford large ring mono or dinuclear complexes (section 3.1, figure 3.1) when bidentate α,ω-diphosphines $Bu^t_2P(CH_2)_xPBu^t_2$ (x = 9, 10) are used.[19]

An attempt to carry out this reaction using the phosphino-ether L_2 gave complex mixtures of products* which could not be separated. The product mixtures produced were variable, depending upon :

(i) The length of time CO was passed through the chloroiridic acid solution prior to the addition of L_2.

* As shown by multiple 'CO' absorptions in the i.r. spectrum.

(ii) The solvent used (MeOH, EtOH, ethoxyethanol).

(iii) The temperature at which L_2 was added to the carbonylated chloroiridic acid solution.

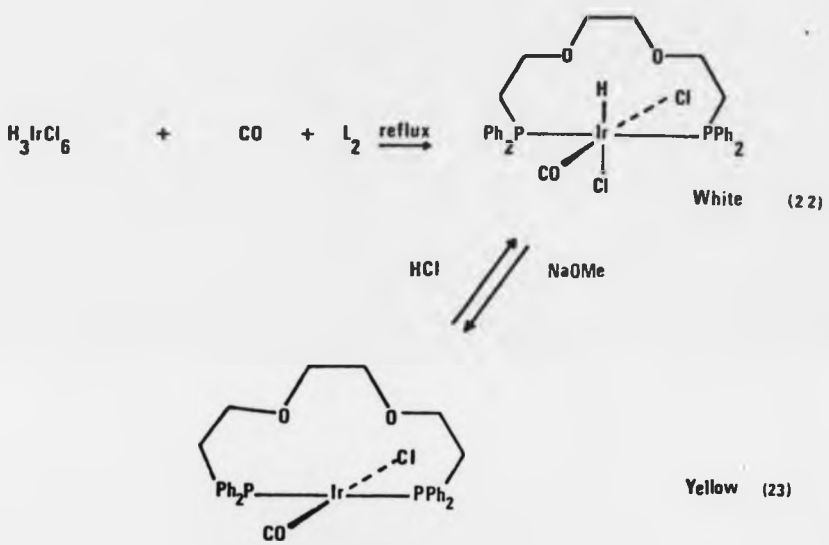


FIGURE 3.5.1.

Optimum conditions were established when CO was passed through a refluxed solution of chloroiridic acid in ethoxyethanol until a straw coloured solution with a faint green tinge* had been obtained. Addition of an equimolar quantity of L_2 at 20^o, followed by 30 minutes reflux, gave a bright green solution from which a cream/white product was obtained on cooling to -10^o. This was identified as $IrHCl_2(CO)(L_2)$ (22) (figure 3.5.1). The bright yellow complex $IrL_2(Cl)(CO)$ (23) was prepared by dehydrohalogenation of (22) with sodium methoxide in MeOH and was oxygen sensitive. An oxygenated benzene solution of $IrL_2(Cl)(CO)$ gave a cream/beige precipitate, not yet fully characterised, but believed to be an oxygen adduct of the

* Other workers[51, 52, 56] use the initially formed straw coloured solution; in this case this is not satisfactory.

type $IrL_2(Cl)(CO)(O_2)$.

The ^1H n.m.r. and i.r. spectra of $IrHCl_2(CO)(L_2)$ both show the expected ligand resonances. The value of the carbonyl frequency [$\nu(CO) = 2040\ cm^{-1}$ (nujol)] is somewhat high when compared with the values for other $IrHX_2(CO)(R_3P)_2$[51] complexes (ca. $2010\ cm^{-1}$) and is closer to the value observed for $RhL_2Cl(CO)(HCl)$* , $\nu(CO) = 2080\ cm^{-1}$.

$\nu(Ir-H) = 2205\ cm^{-1}$ is as expected for an octahedral complex, being similar to the values observed for $IrHX_2(CO)(Ph_3P)_2$.[51] It has been noted[51,52] that high values of $\nu(Ir-H)$ ($\geq 2250\ cm^{-1}$) are found for hydrogens which tend to be eliminated as protons. (22) requires treatment with sodium methoxide in MeOH to remove HCl and in this respect mirrors the stability of $IrHCl_2(CO)(PBu^tMe_2)_2$, for which $\nu(Ir-H) = 2208\ cm^{-1}$. As expected, the infrared spectrum shows two values of $\nu(Ir-Cl) = 310,\ 260\ cm^{-1}$ (cf. $IrHCl_2(CO)(Ph_3P)_2$, $\nu(Ir-Cl) = 310,\ 261\ cm^{-1}$). Further work will be necessary to establish the exact geometry at the metal, but it is thought that the similarity of the spectral data to that of other known octahedral iridium complexes infers that L_2 acts as a trans bidentate ligand with the configuration shown.

$IrL_2(Cl)(CO)$ (23) could not be obtained pure and showed signs of having occluded MeOH or H_2O present ($\nu(OH) = 3450$, broad, nujol); in addition there was a weak unidentified band at $1600\ cm^{-1}$. Ir (nujol) showed no evidence of Ir-H and $\nu(CO) = 1950\ cm^{-1}$, whilst again somewhat higher than typically observed for complexes of the type trans $IrCl(CO)(Ph_3P)_2$ (ca. $1930\ cm^{-1}$), was quite close to the value of $1940\ cm^{-1}$ observed in the complex trans $IrCl(CO)(Bu^tBu^n_2P)_2$.[51] Similarly, $\nu(Ir-Cl) = 310\ cm^{-1}$ was as expected for Cl trans to CO. (23) is bright yellow and shows an absorption maximum at 425 nm with $\epsilon_m \simeq 600$ (CH_2Cl_2). This is typical[51] of an Ir(I) species and contrasts with the Ir(III) precursor (22) which is colourless and does not absorb in this region. (23) reacts readily with dry HCl gas at ambient temperature and pressure in benzene to give (22). Accordingly, (23) is formulated as the trans square planar adduct shown and is believed to be analogous to $RhL_2(Cl)(CO)$, (7).

The formation of a stable HCl adduct shows that the iridium complex (23) has the expected marked increase in oxidative reactivity when compared with

* formed in equilibrium with RhL_2ClCO when the latter is treated with dry HCl.

$RhL_n(Cl)(CO)$. As such, these complexes should be worthy of further study. However, the low yields obtained in the initial reaction of L_n with H_3IrCl_6 and also the extreme difficulty in obtaining consistent and repeatable results, calls for a more efficient synthetic route before such work can be undertaken.

3.5.2 Method C : Preparation of $IrL_1(Cl)(C_2H_4)$ and $IrL_1(Cl)(C_2H_4)(O_2)$

Introduction

The investigation of $IrL_n(Cl)(CO)$ complexes met with limited success due to the synthetic route chosen. As an alternative, the preparation of ethylene complexes of the type $IrL_n(Cl)(C_2H_4)$ was investigated. The complex trans $IrCl(C_2H_4)(Ph_3P)_2$, (I) is known to be reactive towards oxidative addition. For example, reaction with O_2 or SO_2 readily gives the five coordinate addition products $IrCl(C_2H_4)(Ph_3P)_2(X)$ where $X = O_2$ or SO_2.[31] In contrast to the corresponding rhodium system, (I) does not lose ethylene in solution with concomitant dimer formation.[5]

$$2\ \text{trans}\ RhCl(C_2H_4)(Ph_3P)_2 \xrightarrow{-C_2H_4} [RhCl(Ph_3P)_2]_2$$

Such behaviour is believed to be at least partly responsible for our failure to produce complexes of the type $RhL_n(Cl)(C_2H_4)$, where n = 2 or 3, and also made isolation of $RhL_1(Cl)(C_2H_4)$ difficult. Accordingly, L_n analogues of (I) should be stable but reactive species. Furthermore, treatment of (I) with CO gives Vaska's compound[30] and, depending upon the ease of formation of $IrL_n(Cl)(C_2H_4)$ might offer a good route to the analogous CO complexes $IrL_n(Cl)(CO)$.

A number of established methods exist for the preparation of (I). For example, two quite general methods involve displacement of cyclooctadiene or ethylene from $[Ir(C_8H_{14})Cl]_2$ and $[Ir(C_2H_4)_2Cl]_2$ respectively.

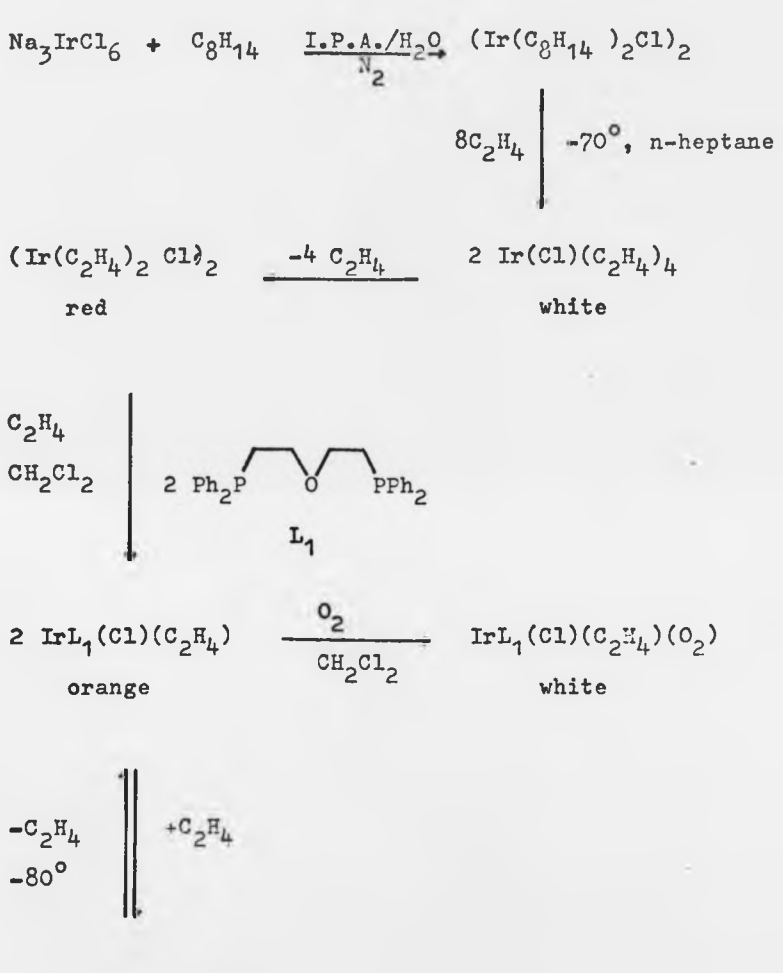
$$[Ir(C_8H_{14})Cl]_2 + 4Ph_3P \xrightarrow{C_2H_4} 2Ir(Cl)(C_2H_4)(Ph_3P)_2 \quad (I) \qquad 31$$

and

$$[Ir(C_2H_4)_2Cl]_2 + 2Ph_3P \longrightarrow [Ir(Cl)(C_2H_4)(Ph_3P)]_2 \xrightarrow{2Ph_3P} \text{trans}\ 2Ir(Cl)(C_2H_4)(Ph_3P)_2 \quad (I) \qquad 57-58$$

The high yield and easy work-up procedure in the latter reaction encouraged an investigation of the analogous reaction with the phosphino-ether L_1, as shown in figure 3.5.2.

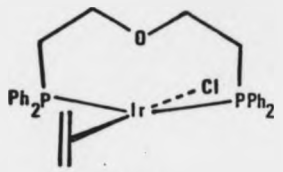
Figure 3.5.2. The Preparation and Reactions of $IrL_1(Cl)(C_2H_4)$.



The Reaction of $[Ir(C_2H_4)_2Cl]_2$ with L_1

Treatment of an ethylene saturated acetone solution of $[Ir(C_2H_4)_2Cl]_2$ with L_1 in ethylene saturated CH_2Cl_2 (1 :2 molar ratio) gave, on cooling to -80°, an orange precipitate $IrL_1(Cl)(C_2H_4)$, (24). This was stable under vacuum or nitrogen but was extremely easily oxidised in air or O_2, forming a white O_2 adduct. (24) is only moderately soluble in CH_2Cl_2 and CH_3Cl_3, giving orange solutions which appear

to decompose on standing. I.r. (nujol) confirmed the presence of L_1 and very closely resembled the spectrum of $RhL_1Cl(C_2H_4)$, (19), far i.r. showed $\nu(Ir - Cl) = 300\,cm^{-1}$ and ^1H n.m.r. the expected L_1 bands . The band corresponding to C_2H_4 is difficult to locate but is believed to be a medium broad band at ca. $\delta = 2.8$ p.p.m. partially obscured by the C(1) methylene signal of L_1 at $\delta = 3.0$ p.p.m. The spectroscopic data resembles that of trans $Ir(Cl)(C_2H_4)(Ph_3P)_2$ [31,57,58] and a distorted trans square planar geometry is tentatively assigned, similar to that in $RhL_1(Cl)(C_2H_4)$. A solution of (24) in $CHCl_3$ does not lose (C_2H_4) on sweeping



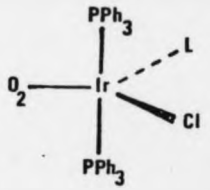
(24)

Bright ORANGE Solid

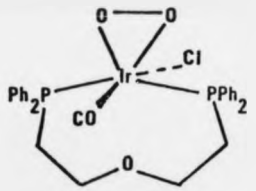
with dry N_2; however, on saturation with (C_2H_4) at -80^o, the orange colour is discharged only to reappear on sweeping with dry N_2. This behaviour is similar to that observed in the reversible formation of $IrCl(C_2H_4)_2(Ph_3P)_2$ from (I), [31] and possibly indicates the reversible formation of $IrL_1(Cl)(C_2H_4)_2$, although there is no other evidence to support this suggestion.

A CH_2Cl_2 solution of (24) reacts rapidly with dry O_2 at ambient temperature and pressure to give a white oxygen adduct $IrL_1(Cl)(C_2H_4)(O_2)$, (25). Van der Ent reported[31] that $IrCl(C_2H_4)(Ph_3P)_2$, (I), reacts with O_2 forming triphenylphosphine containing products but that in the presence of one or more equivalents of free C_2H_4 the diamagnetic oxygen adduct $IrCl(C_2H_4)(Ph_3P)_2(O_2)$ was rapidly formed. He suggested that the reaction might proceed via the unstable bis (ethylene) adduct $IrCl(C_2H_4)_2(Ph_3P)_2$. Dissociation of one ethylene ligand could then produce a reactive non-planar four coordinate intermediate, which he supposed might react fast with O_2 before adopting the less reactive square planar form. In contrast, (24) reacts very readily with O_2 both in solution and in the solid state, without the requirement for free ethylene. If Van der Ent is correct in believing that a non-planar four coordinate compound would react much faster with O_2, this would explain the behaviour of (24) which, in its normal state, must suffer a considerable tetrahedral distortion from square planarity due to the constraint of binding L_1 trans without O donation to the metal.

The addition of O_2 to (24) is irreversible and (25) neither loses O_2 nor C_2H_4 under vacuum (2 days at 20° and 10^{-3} mm Hg). (25) has very low solubility in most organic solvents and was characterised by i.r. and analysis only. I.r. (nujol) showed no bands attributable to phosphine oxides and the spectrum closely resembled that of the precursor (24). A new medium intensity band at 820 cm^{-1} is believed to be $\nu(Ir\langle^{O}_{O})$, and $\nu(Ir-Cl)$ is at 310 cm^{-1}. This contrasts with the values observed for $IrCl(C_2H_4)(Ph_3P)_2(O_2)$ for which $\nu(Ir\langle^{O}_{O}) = 880\ cm^{-1}$ and $\nu(Ir-Cl) = 307\ cm^{-1}$, and may reflect a different geometry for (25). The O_2 adduct of Vaska's compound has the trigonalbipyramidal structure shown[46] and $IrCl(C_2H_4)(Ph_3P)_2(O_2)$ is believed to be similar.[31] (25) cannot adopt this geometry due to the constraint of the bidentate ligand chain nor (as was noted in section 3.2.1) can it act as a trans bidentate donor across the base of a tetragonal pyramid as observed in SO_2 complexes of the



L = CO , C_2H_4



(25)

type $IrCl(CO)(Ph_3P)_2(SO_2)$. It is very tentatively suggested that the structure might lie between these extremes as shown, being similar to the structure postulated for $RhL_1(Cl)(CO)(SO_2)$. The structure of (25) is therefore thought to lie between the extremes of trigonal bipyramidal and tetragonal pyramidal geometry.

SECTION 3.6

Conclusion

The neutral complexes $RhL_n(Cl)(CO)$ have been prepared and afford rare examples of 8, 11 and 14 membered chelate rings, in which there appears to be no very significant interaction between O donors in the ligand chain and the metal atom. The chemistry of these complexes closely resembles that of the known complex trans $RhCl(CO)(Ph_3P)_2$ with some evidence of steric hindrance further reducing reactivity (e.g. the low stability of the SO_2 adducts). The yields of (1), (7) and (8) were good (typically ca. 80%) and no very marked reduction in yield was observed with increasing chain length. In view of the relative ease with which (1), (7) and (8) were prepared, there can be no inherent instability in medium and large ring complexes of this type, and there is no obvious reason why the analogous 17 and 20 membered chelates $RhL_n(Cl)(CO)$ (where $L_n = Ph_3P(CH_2CH_2O)_nCH_2CH_2PPh_3$, n = 4,5) should not be prepared by the same route. Yields of medium to large ring complexes are typically modest; the high yields observed here may be due to a number of factors :

(i) The presence of heteroatoms in L_n will reduce non-bonded H - H interactions and produce a more flexible ligand chain.

(ii) The polar O-donors may favourably effect chain binding in the transition state.

(iii) The CO displacement reaction used may facilitate the formation of large ring chelates since attempts to prepare analogous Ir complexes by the route used for the α,ω-diphosphines also gave poor yields and a mixture of products.

Treatment of (1), (7) or (8) with $AgPF_6$ readily gave good yields of the cations $[RhL_n(CO)(S)]^+PF_6^-$. In these complexes the importance of the ligand O-donors is very apparent. The cations are very stable, reflecting the chelation of either L_n O-donors (n = 1,2) or hydrogen bonded solvent molecules (n = 2,3). Crystal structure data support the belief that the driving force for solvent incorporation derives from the minimisation of H . . . H non-bonded interactions in the ligand chain. Furthermore, the solvent specificity observed depends upon the formation of hydrogen bonds between O-donors of the ligand chain and protons of the solvent molecule. The chemistry of these cations is in some respects similar to

that of the known cationic solvate $[RhCO(Ph_3P)_2(S)]^+$ but the constraint of using a diphosphine appears to prevent the formation of five coordinate adducts analogous to $[RhCO(diene)(Ph_3P)_2]^+$.

Attempts to prepare potentially more reactive complexes of the type $ML_n(Cl)(X)$ where M = Rh, Ir and X = CO, C_2H_4, have met with limited success. $RhL_1(Cl)(C_2H_4)$ was isolated with difficulty due to the ready loss of C_2H_4 and concomitant dimer formation. Furthermore, $RhL_n(Cl)(C_2H_4)$ could not be prepared by the same route, namely ethylene displacement from $[Rh(C_2H_4)_2Cl]_2$, which may be related to the lability of ethylene in this system. In contrast, clean displacement of ethylene occurs on treating $[Ir(C_2H_4)_2Cl]_2$ with L_1, giving the stable complex $IrL_1(Cl)(C_2H_4)$. This reaction appears to be a good route to the series of complexes $IrL_n(Cl)(C_2H_4)$ (n = 2, 3) which are worthy of further investigation.

SECTION 3.7

Experimental Section

The precious metal compounds $RhCl_3 \cdot 3H_2O$, Na_3IrCl_6, H_3IrCl_6 and $IrCl_3$ were both purchased from and kindly loaned by Johnson Matthey Limited. All solvents were reagent grade and were dried, purified and stored under dry N_2 as previously discussed.* The ligands 'L_n' (n = 1, 2 or 3), $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ were prepared as previously described* and were used as stock solutions in degassed CH_2Cl_2 or benzene (1 mmole ≡ 1 ml). Complexes were routinely prepared in degassed solvents and isolated under a dry N_2 atmosphere. The solid complexes were generally air stable except where noted.

Instrumentation was as previously described with the following additions. Conductivity measurements were made at $25^o \pm 0.1^o$ on 10^{-3} M acetone solutions using a Philips conductivity cell and a Wayne Kerr Universal Bridge. Values are quoted as Λ_m = (ohm)$^{-1}$ (cm)$^{-1}$ (litre) (equivalent)$^{-1}$. Molecular weights were determined by Vapour Pressure Osmometry on ca. 10^{-3} M solutions $(CH_2Cl)_2$ by Bernhardt Limited. Cryoscopic molecular weights were determined for 10^{-3} M benzene solutions using a Beckmann thermometer reading to $\pm 0.01^o$.

Some difficulty was encountered obtaining accurate analytical figures, particularly of PF_6^- containing complexes. Other workers have experienced similar difficulties, e.g. see reference 9 page 4205, specifically their reference 47 and references therein. In particular, phosphorus analysed consistently too high. For example, a sample of $[RhL_1(CO)]^+PF_6^-$ of proven spectral, crystallographic and visual** integrity gave P (calculated) = 12.95 and P (found) = 16.92.

Preparation of Complexes

$[Rh(C_2H_4)_2Cl]_2$ and $[Ir(C_2H_4)_2Cl]_2$ were prepared by standard literature methods.

Tetracarbonyl Dirhodium Dichloride

This was prepared as described in Inorganic Synthesis VII, page 211, with some variation in the isolation procedure. $RhCl_3(3 \cdot H_2O)$ on a sinter was treated with CO at 100^o for 5 hours (yields were improved when CO was first saturated with

* See Experimental Section, Chapter 2

** The crystals sent for analysis were inspected under the microscope for adhering foreign matter.

H_2O at 100°). Approximately 50% of the product sublimed up the sides of the apparatus as beautiful orange needles, leaving a brown/orange solid on the sinter. Extraction of this solid with CH_2Cl_2, filtration through celite and removal of CH_2Cl_2 in vacuo gave a further crop of orange needles. There was thus obtained tetracarbonyl dirhodium dichloride 3.1 g , 85% as orange needles. I.r. (nujol : 460 - 200 cm^{-1}) : 435 (m), 300 (sh), 284 (vs), 274 (vs), cf. the same values reported in Inorg.Chem., 1967, 6 No. 9, 1647.

$RhL_1(Cl)(CO)$ (1)

Tetracarbonyl dirhodium dichloride (0.44 g, 1.13mmole) in MeOH (25 ml, 0°) was treated with $Ph_2P(CH_2CH_2O)_1CH_2CH_2PPh_2$ (L_1), (2.26 ml of stock solution ; 2.26mmole). A slightly oily yellow precipitate was immediately formed and the resulting mixture was stirred overnight at 20°. The precipitate was filtered, triturated with MeOH (4 x 5 ml) and redissolved in the minimum of CH_2Cl_2 ; progressive addition of MeOH over 3 hours and cooling to -20° afforded yellow microcrystalline needles, recrystallisation being completed by the addition of ether.* These were filtered and dried in vacuo (20°, 2 days). There was thus obtained chlorocarbonyl 1,5 bis(diphenylphosphino)-3-oxa pentane rhodium (I), 1.25 g, 91% as air stable yellow needles which decomposed above 170°. Soluble : CH_2Cl_2, $CHCl_3$, benzene ; insoluble : MeOH, Et_2O, alkanes. N.m.r., i.r. and analytical details are reported in text. The visible/u.v. spectrum shows a peak at λ_m = 364 n.m. with $\epsilon_m \simeq 3230$. The complex is neutral Λ_m (acetone) = 13.9. Cryoscopy on 10^{-3} M solutions in benzene gave an average value for the molecular weight of 704 ± 100 (cf. expected value : monomer = 608.5, dimer = 1217.0) for two successive determinations.

$RhL_2(Cl)(CO)$ (7)

This was prepared as above from $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$, ($L_2$), (3.09 ml of stock solution, 3.09 mmole) and tetracarbonyl dirhodium dichloride (0.6 g, 1.54 mmole). There was thus obtained chlorocarbonyl 1,8 bis(diphenylphosphino)-3,6-dioxa octane rhodium (I), 1.75 g, 87% of a yellow, air stable, microcrystalline solid, decomposing above 152°. Spectral and analytical data is presented

* A low yield of microcrystalline material has been obtained by slow evaporation of a CH_2Cl_2 solution. This is currently being investigated with a view to single crystal X-ray structure determination.

in text. The visible/u.v. spectrum showed a major peak at λ_m = 360 nm with $\epsilon_m \simeq 3000$. The complex is neutral Λ_m (acetone) = 12.2. Cryoscopic molecular weight = 734 ± 100 (cf. expected values : monomer = 652.5, dimer = 1305) for one determination.

Rh L_3(Br)(CO) (2)

The bromide complex was prepared similarly, except that $[Rh(CO)_2Cl]_2$ was refluxed (under CO) for 15 minutes in MeOH with a ca. twenty-fold excess of lithium bromide before adding the ligand to the cooled solution. After stirring overnight, the resulting treacle-like yellow/orange solid was washed with MeOH and subjected to several freeze/thaw cycles (20° to -180°) with vigorous agitation, affording a fine bright yellow powder. Recrystallisation from boiling EtOH afforded bromocarbonyl 1,5 bis (diphenylphosphino)-3-oxa pentane rhodium (I), 80% as a yellow microcrystalline powder. Infrared (nujol) : ν(CO) = 1960 cm^{-1}, no bands observed for ν(Rh - halogen) down to 200 cm^{-1}.

Rh L_1(CO)(I) (3)

The attempted preparation was similar except Rh L_1(Cl)(CO), (1), prepared in situ, was refluxed for 10 minutes with a ten-fold excess of lithium iodide in $MeOH/CH_2Cl_2$. Solvent was removed in vacuo and the resulting sticky orange/brown solid was triturated with MeOH, giving a deep yellow/orange powder. Recrystallisatio from $EtOH/CH_2Cl_2$ at -80° gave 20% of a deep yellow solid with spectra analogous to Rh L_1(CO)(X) (X = Cl, Br), although analytical results were very poor (5% error in C analysis). A benzene solution of Rh L_1(CO)(I) rapidly reacted with dry oxygen affording an insoluble beige/brown solid with ν(Rh - O_2) = 885 cm^{-1} (nujol).

Rh L_1(CO)(NCS) (4)

A solution of Rh L_1Cl CO (0.105 g, 1.73 mmole) and NH_4SCN (0.0263 g, ca. 1 molar excess) in $MeOH/CH_2Cl_2$ (10 ml, 50:50) was stirred overnight at 20°. The resulting bright yellow solution was extracted with (3 x 5 ml) of water and the CH_2Cl_2 phase was dried over anhydrous sodium sulphate. The volume of solvent was reduced to ca. 4 ml and ether was added until the solution became faintly turbid. Slow cooling to -80° gave yellow needles which were collected and dried in vacuo. There was thus obtained carbonyl, isothiocyanato 1,5 bis (diphenylphosphino)-3-oxa pentane rhodium (I), (4), 0.11 g, 98% as air stable yellow needles. For $C_{30}H_{28}N_1O_2P_2Rh_1S_1$, calculated : C, 57.04; H, 4.44; N, 2.22. Found : C, 57.12; H, 4.37; ^{1}H n.m.r. ($CDCl_3$): 2.9 (s, 4H), 4.2 (s, 4H), ca. 7.2 (m/o, p doublet 20H).

I.r. (nujol) : ν(CN) = 2085, ν(CS) = 840, ν(CO) = 1985, 2005, ν(COC) = 1095 cm^{-1}. The crystals were soluble in CH_2Cl_2, $CHCl_3$ and benzene and insoluble in MeOH, Et_2O and alkanes. The complex was neutral Λ_m = 14.5 (acetone at 25°) and 10^{-3} M solution.

$RhL_2(CO)(NCS)$

This was similarly prepared as a crystalline yellow solid which was characterised by spectra only. I.r. (nujol) : ν(CN) = 2085, ν(CS) = 840, ν(CO) = 1990 2005 cm^{-1}. All bands strong and sharp except ν(CS) medium. ^{1}H n.m.r. ($CDCl_3$) : 3.1 (br, s, 4H), 4.1 (br, s, 4H), 3.5 (br, s, 4H), ca. 7.2 (aromatic protons, 20H).

Reaction of $RhL_1(Cl)(CO)$ with SO_2

Dissolution of $RhL_1(Cl)(CO)$ in neat liquid SO_2 and subsequent removal of SO_2 at ca. -10° with a stream of N_2 gas, gave a yellow crystalline solid. This lost SO_2 rapidly even at -10°. A nujol mull of the freshly prepared solid showed fairly strong bands attributable to an S-bonded SO_2 group : $\nu(SO_2$, symm.) = 1060, $\nu(SO_2$, assym.) 1220, 1190 cm^{-1}; in addition two CO bands were observed at 1975 and 2030 cm^{-1} corresponding to $RhL_1(Cl)(CO)$, (1), and $RhL_1(Cl)(CO)(SO_2)$, (5), respectively.

Similar reactions were observed when $Rh(L_2)(Cl)(CO)$ and $Rh(L_3)(Cl)(CO)$ were treated with SO_2. Again, the equilibrium constant for SO_2 uptake favours rapid loss of SO_2 and no solid complexes suitable for analysis could be isolated.

Reaction of $RhL_2(Cl)(CO)$ and HCl

As discussed in text, (1) undergoes an equilibrium reaction with HCl gas in dry CH_2Cl_2 solution. (1) has an absorption at λ_m = 364 n.m. whereas the HCl adduct $RhL_1(Cl)(CO)(HCl)$, (6), does not. Accordingly, an estimate of K for the reaction :

$$RhL_1(Cl)(CO) + HCl \xrightarrow{K} RhL_1(Cl)(CO)(HCl) \qquad (6)$$

was obtained by monitoring the absorbance at 364 n.m. for known equilibrium mixtures. Allowance was made for the component of the new band due to (6) ($\lambda_m \sim 308$) contributing at 364 and also for a slow side reaction, which caused loss of intensity of the band at 364 n.m. (this typically did not exceed 0.005 absorbance units per minute).

Stock solutions of (1) (0.6810×10^{-3} M) and HCl* (0.1415 M) were prepared in dry CH_2Cl_2. These were stored under nitrogen in septum sealed flasks and

* Standardised by titration immediately prior to use.

thermostated at 20°. The standard HCl solution in CH_2Cl_2 was prepared in one litre quantities, stored in very full vessels to minimise both loss of HCl gas and contamination with H_2O. Measured volumes of reactants were transferred by syringe to a septum sealed u.v. cell (silica, 1 cm) which had previously been flushed with dry nitrogen. The absorbance at 364 n.m. , was recorded at one minute intervals over 10 minutes and the true absorbance at mixing time determined by back extrapolation. Results are presented in table 3.8.1. A further check on the value of K thus obtained was made by monitoring the carbonyl resonances of (1) and (6) in the i.r. spectrum. This gave an order of magnitude estimate of $K \simeq 10$.

TABLE 3.8.1

Equilibrium Constant Data for
$RhL_1(Cl)(CO) + HCl \rightleftharpoons RhL_1(Cl)(CO)(HCl)$

Initial conc. $RhL_1(Cl)(CO)$ $\times 10^{-3}$ m/l	Initial conc. HCl m/l	Absorbance at 364 n.m.	Calculated K
0.6009	0.01664	1.725	14.4
0.5675	0.02359	1.585	14.5
0.3405	0.07075	14.2	14.3
			K = 14.4

ϵ_m for $RhL_1(Cl)(CO)$ at 364 = 3230
ϵ_m for $RhL_1(Cl)(CO)(HCl)$ at 364 = 1502

Reaction of $Rh(L_2)(Cl)(CO)$ with HCl

Completely analogous spectra were observed on passing HCl through a CH_2Cl_2 solution of $Rh(L_2)(Cl)(CO)$. i.r. of a solution of (7) (40 mg/ml) in CH_2Cl_2 with a one hundred-fold molar excess of HCl showed : ν(CO) = 1975, 2070 ; ν(Rh - H) = 2200 cm^{-1} (v. weak) or 2100 (medium) cm^{-1}.

An estimate of K for the reaction :

$$Rh(L_2)(Cl)(CO) + HCl \xrightarrow{K} Rh(L_2)(Cl)(CO)(HCl)$$

was obtained as described for (1) from the u.v./visible spectrum. Essential details are tabulated in table 3.8.2.

Completely analogous i.r. and u.v. spectra were observed in the reaction of $Rh(L_3)(Cl)(CO)$ and HCl. K was not determined for this equilibrium.

TABLE 3.8.2

Equilibrium Constant Data for
$Rh(L_2)(Cl)(CO) + HCl \rightleftharpoons Rh(L_2)(Cl)(CO)(HCl)$

Initial conc. $RhL_2(Cl)(CO)$ $\times 10^{-3}$ m/l	Initial conc. HCl m/l	Absorbance at 364 n.m.	Calculated K
0.591	0.0267	1.07	27.8
0.517	0.0476	0.81	28.1
0.490	0.0555	0.725	28.7
			K = 28.2

ϵ_m for $RhL_2(Cl)(CO$ at 364 = 2556
ϵ_m for $RhL_2(Cl)(CO)(HCl)$ at 364 = 806

Preparation and Reactions of the Cations $[RhL_nCO(S)]^+ PF_6^-$

$[RhL_1(CO)]^+ PF_6^-$ (9)

A solution of $Rh(L_1)(CO)(Cl)$ (0.647 g, 1.05mmole) in CH_2Cl_2/acetone (30 ml, 1 :1) was treated with a solution of $AgPF_6$ (0.268 g, 1.06mmole) in acetone (10 ml) at 20°. Immediate and quantitative precipitation of AgCl occurred. The solution was filtered through celite and solvent was removed in vacuo. The resulting bright yellow solid was dissolved in the minimum of CH_2Cl_2 and hot MeOH was added until faint turbidity was observed. Cooling to 20° gave beautiful bright yellow prisms, recrystallisation being completed by addition of ether and cooling to -80°. A lower yield of crystals suitable for single crystal X-ray work was obtained from MeOH as the only solvent (see the experimental section of Chapter 4). There was thus obtained: carbonyl 1,5 bis(diphenylphosphino)-3-oxa pentane rhodium (I) hexafluorophosphate, (9), 0.64 g, 84%, as yellow prisms which are indefinitely stable

in air at 20° but decompose rapidly above 80°. Solutions of (9) in MeOH, CH_2Cl_2 or $CHCl_3$ were stable at 20° but rapidly decomposed above 40°, giving unidentified material. (9) was soluble in acetone, CH_2Cl_2, $CHCl_3$ and benzene, slightly soluble in MeOH, Et_2O and EtOH and insoluble in alkanes. Conductivity was typical of a cationic complex Λ = 144.8 (acetone at 25°, 10^{-3} M solution). Spectra and analytical data are presented in text.

$[RhL_1CO]^+ BF_4^-$ (10)

This was prepared as above from $Rh(L_1)(Cl)(CO)$ and $AgBF_4$; yield, 80% of a bright yellow microcrystalline complex. I.r. (nujol) : ν(CO) = 2000 (s), ν(C - O - C) = 1100 (m), $\nu(BF_4^-)$ = 1100 cm^{-1} (br). The preparation of a BF_4^- complex offered no advantages and since complexes having such anions are frequently reported as solvates, PF_6^- has been used as the preferred counterion.

$[RhL_2CO(S)]^+ PF_6^-$ (15)

This was prepared as above from $Rh(L_2)(Cl)(CO)$ (0.824 g, 1.3mmole) and $AgPF_6$ (0.319, 1.3mmole). Recrystallisation from MeOH / CH_2Cl_2 gave yellow prisms which were washed with ice-cold MeOH and dried in vacuo for 3 days at 20°. There was thus obtained $[Rh(L_2)(CO)(MeOH)]^+PF_6^-$ (15), 0.75 g, 75%, in which one molecule of MeOH occupies the fourth coordination site at the metal. Physical properties were as described for $[Rh(L_1)(CO)]^+ PF_6^-$; spectral and analytical data are reported in text.

The reaction was repeated (CH_2Cl_2 in the absence of all O-donor solvents) and the amorphous yellow powder obtained was reprecipitated from CH_2Cl_2 by addition of hexane and cooling to 0°. There was thus obtained $[Rh(L_2)(CO)]^+ PF_6^-$ (14) as a yellow powder. I.r. (nujol) and ^1H n.m.r. (acetone) showed no evidence of coordinated solvent.

$[RhL_3CO(H_2O)]^+ PF_6^-$

This was prepared similarly from $Rh(L_3)(Cl)(CO)$ (0.721 g, 1.03mmole) and $AgPF_6$ (0.262 g, 1.03mmole) and, despite synthesis under ostensibly dry conditions, the resulting yellow, highly crystalline material contained one water molecule per molecule of complex. This was not removed by pumping in vacuo (10^{-4} mm, 20°) for one week. Spectral and analytical data is reported in text. Yield 0.63 g, 74%.

The reaction has been repeated with particular attention being paid to the exclusion of water but an aquo complex was still obtained.

The Reaction of $[RhL_1CO]^+ PF_6^-$ and NH_4SCN

$[RhL_1CO]^+ PF_6^-$ (0.115 g, 0.16mmole) in acetone (1 ml) was treated with NH_4SCN (0.0122 g, 0.16mmole) in acetone (1 ml). A yellow solid was immediately precipitated. This was filtered and triturated with MeOH (3 x 5 ml) to remove excess NH_4SCN and NH_4PF_6. The product was dissolved in CH_2Cl_2 (4 ml) and filtered through celite to remove traces of a fine white solid. The solvent volume was reduced to ca. 0.5 ml in vacuo and diethyl ether was added dropwise until faint turbidity was noted. On cooling to 0° yellow needles were obtained (a further crop being obtained by stepwise addition of pentane); these were filtered, washed with ether and dried in vacuo. There was thus obtained $RhL_1(CO)(NCS)$, (4), ca. 0.1 g, ~100%, as an air stable solid. This was soluble in CH_2Cl_2, $CHCl_3$ and benzene, slightly soluble in acetone and insoluble in MeOH and Et_2O. The complex was neutral, $\Lambda \simeq 15$ (acetone at ca. 20°). I.r. (nujol), identical with the product obtained by the slow exchange between RhL_1ClCO and NH_4SCN (vide infra). Similarly prepared were $RhL_2(CO)(NCS)$ and $RhL_3(CO)(NCS)$. These were identified by i.r. spectra only.

Reaction of $[RhL_1CO]^+ PF_6^-$ with Ph_3P

Treatment of a solution of $[RhL_1CO]^+ PF_6^-$ (0.11 g, 0.15mmole) in ether (5 ml) with Ph_3P (0.0401 g, 0.15mmole) in ether (5 ml) gave an immediate colour change from deep yellow to pale yellow. Removal of ether in vacuo followed by recrystallisation from hot MeOH gave $[RhL_1CO(Ph_3P)]^+ PF_6^-$ (11), 0.14 g, 90%, as a yellow microcrystalline solid. Calculated for $C_{47}H_{43}F_6O_2P_4Rh_1$: C, 57.55; H, 4.39; P, 12.65. Found : C, 57.13; H, 4.28; P, 13.28. I.r. (nujol) : $\nu(CO)$ = 1995, $\nu(PF_6)$ = 835, and unshifted L_1 bands. ^1H n.m.r. ($CDCl_3$) : 2.9 (broad singlet, 4H), 4.15 (broad singlet, 4.2H), ca. 7.2 (aromatic, 36.2H).

Reaction of $[RhL_1CO]^+ PF_6^-$ with SO_2

SO_2 was passed through a solution of $[RhL_1CO]^+ PF_6^-$ in CH_2Cl_2 for 2 minutes at 20°. I.r. (CH_2Cl_2) showed new bands at 2040, 1220, 1195 and 1060 cm^{-1} as well as bands corresponding to $[Rh(L_1)(CO)]^+ PF_6^-$. The u.v./visible spectrum (CH_2Cl_2) showed a maximum at 315 n.m., extending to the base line at around 440 n.m.

No solid adduct could be isolated from the equilibrium mixture.

Reaction of $[RhL_1CO]^+ PF_6^-$ with HCl

HCl gas was bubbled through a CH_2Cl_2 solution of $[RhL_1CO]^+ PF_6^-$, (9), for 2 minutes. Apart from bands due to (9), new i.r. bands were observed at 2100 (m)

and 2080 (s). The u.v./visible spectrum appeared unchanged on passage of HCl gas and indicated maxima beyond the cut of limit at 230 n.m. . Shoulders were observed at 270 and 275 nm. respectively. No solid complex can be isolated.

$RhL_1(Cl)(C_2H_4)$ (19)

To a stirred slurry of $[Rh(C_2H_4)_2Cl]_2$ (0.30 g, 0.771 mmole) in ethylene saturated $MeOH/CH_2Cl_2$ (25 ml of a 1 :1 mixture) was added L_1 (1.54 ml, 1.54 mmole of stock solution). The brown dimer dissolved rapidly affording a pale yellow/orange solution. The temperature was reduced to ca. 10° and CH_2Cl_2 was slowly evaporated over 3 - 4 hours with a vigorous stream of C_2H_4. A bright yellow precipitate gradually formed,was filtered off under C_2H_4 and dried in a stream of C_2H_4 gas. There was thus obtained $RhL_1(Cl)(C_2H_4)$, (19) (0.49 g, 52%) as a bright yellow powder. This was not analysed due to ready loss of C_2H_4. ^1H n.m.r. ($CDCl_3$) showed L_1 peaks at 2.9 (br, s, 4H), 4.15 (br, s, 4H) ca. 7.2 (aromatic, 20H) and a broad band at 3.5 p.p.m. attributed to ethylene. This had an integral almost equivalent to 4H for a freshly prepared solution (or one saturated with C_2H_4). I.r. (nujol) shows the expected L_1 bands as in (1) with the addition that ν(Rh - Cl) = 310 cm^{-1}.* The u.v./visible spectrum of a CH_2Cl_2 solution of (19) saturated with C_2H_4 has a maximum at λ = 359 nm., (19) is not oxygen sensitive but readily loses ethylene with dimerisation when dissolved in CH_2Cl_2, $CHCl_3$ or benzene. It is insoluble in MeOH, EtOH, Et_2O and alkanes. On heating in vacuo C_2H_4 is rapidly lost above 40° and more slowly at 20° (ca. 2 hours at 10^{-3} mm Hg).

$[RhL_1Cl]_2$ (20)

This is readily obtained as described in the preparation of (19) except that the initial pale yellow/orange solution is degassed with dried N_2, affording a deep red/brown solution. Removal of most of the CH_2Cl_2 in vacuo with the volume maintained by addition of MeOH, affords a yellow/brown precipitate. This was filtered and dried in vacuo. There was thus obtained $[RhL_1Cl]_2$, (20) in ca. 90% yield as an air stable yellow/brown, microcrystalline solid, decomposing above 170°. (20) may also be obtained by dissolution of (19) in CH_2Cl_2 and removal of solvent in vacuo Analysis : calculated for $C_{56}H_{56}Cl_2O_2P_2Rh_2$: C, 57.88; H, 4.82; P, 10.68; found : C, 57.84; H, 5.20; P, 10.27. ^1H n.m.r. ($CHCl_3$) : 2.85 (br, s, 4H at C(1)), 3.7 (br, s, 4H at C(2)), I.r. (nujol) : ν(bridging chloride) = 300 cm^{-1}.* (20) is soluble in CH_2Cl_2, $CHCl_3$ and benzene.

* Tentative assignments. See text.

$IrH(Cl)_2(CO)(L_2)$ (22)

H_3IrCl_6 (0.204 g, 0.5 mmole) was dissolved in 2-ethoxyethanol (4 ml). Dry CO was bubbled through the refluxed solution. Over 9 - 9½ hours the initial red/brown solution became golden yellow and then straw coloured with a distinct green tinge. The solution was cooled to 20°. L_2 (0.243 g, 0.5 mmole) was added dropwise over 10 minutes and the mixture was then refluxed for a further 30 minutes, affording a bright green solution. On cooling to 20° a cream/white precipitate was obtained. This was filtered and dried in vacuo. There was thus obtained $IrH(Cl)_2(CO)(L_2)$, (22), 0.16 g, 40% as a cream/white solid. Analysis : calculated for $C_{31}H_{33}Cl_2O_3P_2Ir_1$; C, 47.80; H, 4.24; O, 6.17; found : C, 48.15; H, 4.57; O, 5.95. ^1H n.m.r. ($CDCl_3$) : 3.0 (br, s, 4H), 4.25 (br, s, 4H), 3.40 (s, 4H). These peaks are assigned to the methylene protons at C(1), C(2) and C(3) respectively in L_2. I.r. (nujol) : ν(CO) = 2040, ν(Ir - H) = 2205 and ν(Ir - Cl) = 310 and 260 cm^{-1} respectively.

$IrL_2(Cl)(CO)$ (23)

A slurry of $IrH(Cl)_2(CO)(L_2)$ (0.071 g, 0.09 mmole) in MeOH (0.5 ml) was refluxed for 2 minutes with NaOMe (0.0049 g, 0.09 mmole). A bright orange solution was formed. MeOH was removed in vacuo giving a yellow solid. This was dissolved in the minimum of dry ether and pentane was added until faint turbidity was noted. Cooling to -80° afforded $IrL_1(Cl)(CO)$, (23), 60 mg, 88% as a bright yellow microcrystalline powder. I.r. (nujol) showed evidence of impurity, (ν(OH) = 3450 broad) and this was not removed on pumping in vacuo. In addition there was a weak unidentified band at 1600 cm^{-1}. There was no evidence of ν(Ir - H) and ν(CO) = 1950 cm^{-1} with ν(Ir - Cl) = 310 cm^{-1}. U.v./visible spectra showed λ_m = 425 n.m. , $\epsilon_m \simeq$ 600 (CH_2Cl_2). Dry HCl gas was bubbled through a solution of (23) (50 mg) in benzene (2 ml) at 20° for 2 minutes. The resulting colourless solution was evaporated in vacuo giving a white solid, shown to be the HCl adduct (22) by i.r. spectroscopy.

$IrL_1(Cl)(C_2H_4)$ (24)

An ethylene saturated solution of $[Ir(C_2H_4)_2Cl]_2$, (0.1 g, 0.18 mmole) in acetone (5 ml) was treated with $Ph_2PCH_2CH_2OCH_2CH_2PPh_2$ (0.353 ml of stock solution in CH_2Cl_2, 0.35 mmole) in ethylene saturated CH_2Cl_2 (1 ml). An orange precipitate was formed during the addition and precipitation was completed by the addition of pentane (3 ml) and cooling to 0°. The orange solid was collected by

filtration, washed with acetone (0.5 ml at -80^{o}) and pentane (1 ml at 0^{o}) and dried in vacuo. There was thus obtained $IrL_1(Cl)(C_2H_4)$, (24) as an orange powder (yield 0.2 g, 80%). A CH_2Cl_2 or $CHCl_3$ solution of (24) was orange at -80^{o} but became colourless on saturation with ethylene ; the original orange chromophore was restored on nitrogen degassing. (24) was very oxygen sensitive and was characterised by analysis of its oxygen adduct (see below). ^{1}H n.m.r. ($CDCl_3$) showed L_1 peaks at 3.0 (br, s, 4H), 42 (br.s, 4H) and ca. 7.2 (aromatic protons, 20H). A medium broad band at ca. 2.8 p.p.m. is attributed to ethylene. I.r. (nujol) : $\nu(Ir-Cl) = 300\ cm^{-1}$.

$IrL_1(Cl)(C_2H_4)(O_2)$ (25)

Dry oxygen was passed through a solution of $IrL_1(Cl)(C_2H_4)$ (50 mg, 0.07 mmole) in CH_2Cl_2 (1 ml) at 20^{o} for 2 minutes. A white precipitate formed rapidly; this was filtered, washed with CH_2Cl_2 (2 x 0.5 ml at 0^{o}) and dried in vacuo. There was thus obtained $IrL_1(Cl)(C_2H_4)(O_2)$, (25), as a white solid (yield 47 mg, 90%). Analysis : calculated for C, 49.34 ; H, 4.39 ; P, 8.50 ; found : C, 49.37 ; H, 4.43 ; P, 8.10. I.r. (nujol) : $\nu(Ir\langle^{O}_{O}) = 820$ (m), $\nu(Ir-Cl) = 310$ (m) cm^{-1}.

$RhL_3(Cl)(CO)$ (8)

This was prepared as shown previously from $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$, ($L_3$), (1.9 ml of stock solution, 1.89 mmole) and tetracarbonyl dirhodium dichloride (0.367 g, 0.943 mmole). There was thus obtained chlorocarbonyl 1,11 bis (diphenyl-phosphino)-3,6,9-trioxa undecane rhodium (I), 1.2 g, 88%, as a pale yellow air stable solid, decomposing above 172^{o}. Spectral and analytical data are presented in text. The u.v./visible spectrum shows a major peak at $\lambda_m = 360$ n.m. with ϵ_m very approximately = 3000. The complex is neutral $\Lambda_m = 10$ and 13 in successive determinations on separately prepared 10^{-3} M solutions in acetone. Molecular weight was not determined.

SECTION 3.8

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CHAPTER 4

CHAPTER 4

4.1 Discussion of the Crystal Structures of:

4.1.2. Trans[carbonyl][bis 1, 5(diphenylphosphino)-3--oxa-pentane] Rhodium(I) Hexafluorophosphate.

4.1.3. Trans[aquo][carbonyl][bis 1, 11(diphenylphosphino)-3, 6, 9-trioxa-undecane] Rhodium(I) Hexafluorophosphate.

4.1.4. A preliminary report on the structure of Trans[carbonyl] [methanato][bis 1, 8(diphenylphosphino)-3, 6-dioxa-octane] Rhodium(I) Hexafluorophosphate.

4.1.1. Introduction

Single crystal X-Ray Studies have been carried out on the above complexes to unambiguously define their structures and to determine the importance and extent of ligand oxygen involvement in the metal bonding scheme.

The structures of $[RhL_1CO]^+ PF_6^-$ and $[RhL_3CO(H_2O)]^+ PF_6^-$ have been successfully refined to final R values of 0.051 and 0.05 respectively. Complete experimental data and method of solution is included in the second half of the Chapter (Section 4.2). $[RhL_2CO(MeOH)]^+ PF_6^-$ has been refined to a current R value of 0.075* and the structure is reported for comparison with the previous structures. Because of the preliminary nature of this determination only basic crystal and unit cell data and the method of solution are reported in the second half of the Chapter.

* Further refinement is in progress.

4.1.2. The Crystal Structure of $[Rh\ L_1CO]^+\ PF_6^-$

The structure consists of discrete monomeric ions, the PF_6^- counter-ions occupying sites well removed from the metal centres. A perspective view of the cation with labelling scheme is given in Fig. 4.1. Selected bond distances and angles are given in Table 4.1. Complete data on all measured and calculated parameters is included at the end of the chapter. The molecule has spacegroup $P\bar{1}$ and there is no imposed symmetry.

Geometry about the Metal.

The geometry of the coordination polyhedron about the rhodium atom is approximately square planar. The rhodium atom lies 0.003 Å above the plane defined by P(1)-P(2)-O(1)-C(5) and the metal atom itself. Other least square planes computed using only the coordinating atoms show similar small deviations (Table 42). There is a very small distortion towards tetrahedral geometry with P(1) and P(2) lying 0.033 Å and 0.035 Å above the plane and O(1) and C(5) lying 0.038 Å and 0.034 Å below the plane, respectively. The small P(1)-Rh(1)-P(2) bond angle (165.9(1)) is almost entirely accounted for by an in plane distortion for trans geometry for these atoms. This results from the steric inability of this ligand to take an unstrained 180° 'bite'. X-Ray data on Rh(I) complexes of the bidentate ligand dpe show five membered chelate rings having P-Rh-P angles ~83°. Ibers et al[2] have therefore argued that the potentially tridentate ligand bis-(diphenylphosphino-ethyl)-phenyl phosphine might show a trans P-M-P angle of 166° (twice the dpe angle of 83°) and that the large distortion from trans geometry (14°) explains their failure to produce such complexes. Bearing in mind the difference between C-O and C-P bond lengths (1.51 and 1.89 Å respectively) L_1 might be expected to have a trans P-Rh-P angle of ~166°. The agreement between the structure of $[RhL_1CO]^+\ PF_6^-$ and this simple model is surprisingly good in view of the fact that it exhibits the largest in-plane distortion from trans P-Rh-P geometry yet observed. The Rh(1)-P(1) and Rh(1)-P(2) bond distances (average 2.300(2)) are shorter than those observed in comparable triphenylphosphine complexes but only slightly smaller than observed in

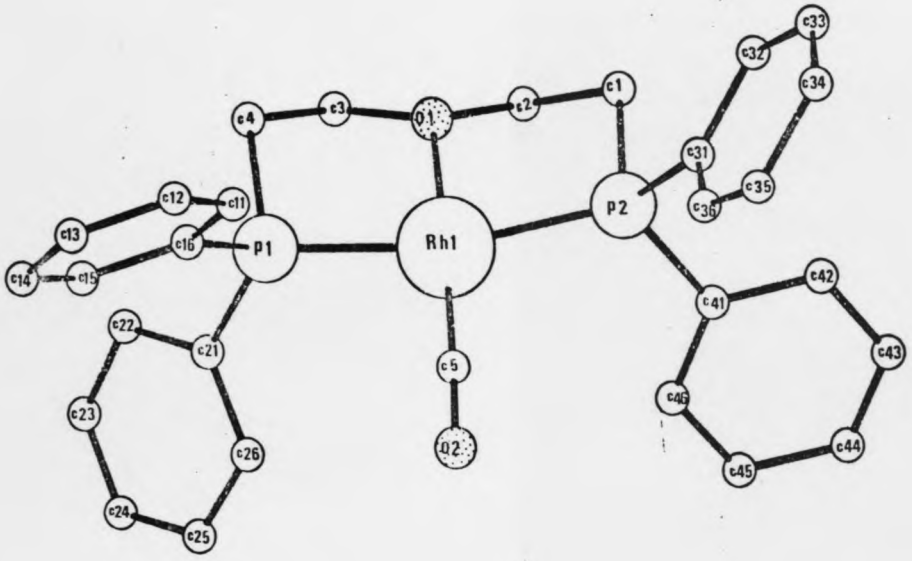


Figure 4.1 The Carbonyl(bis1,5(diphenylphosphino)-3-oxa-pentane)Rh(I) cation in crystals of its salt with hexafluorophosphate anion.

TABLE 4.1

$[RhL_1CO]^+PF_6^-$

Selected Bond Lengths (Å) and Angles (°) *

about rhodium

Rh(1) - P(1)	2.307(2)	P(1)-Rh(1)-P(2)	165.9 (1)
Rh(1) - P(2)	2.294(2)	P(1)-Rh(1)-O(1)	82.9 (2)
Rh(1) - O(1)	2.112(7)	P(1)-Rh(1)-C(5)	99.1 (4)
Rh(1) - C(5)	1.78(1)	P(2)-Rh(1)-O(1)	83.3 (2)
		P(2)-Rh(1)-C(5)	94.9 (4)
		O(1)-Rh(1)-C(5)	175.8 (5)

about phosphorus

P(1)-C(11)	1.82(1)	Rh(1)-P(1)-C(11)	119.6 (4)
P(1)-C(21)	1.83(1)	Rh(1)-P(1)-C(21)	119.8 (4)
P(1)-C(4)	1.85(1)	Rh(1)-P(1)-C(4)	100.6 (4)
P(2)-C(31)	1.83(1)	C(11)-P(1)-C(21)	103.8 (5)
P(2)-C(41)	1.81(1)	C(11)-P(1)-C(4)	106.4 (6)
P(2)-C(1)	1.86(1)	C(21)-P(1)-C(4)	105.0 (6)

about oxygen

Rh(1)-O(1)-C(2)	117.1(7)	Rh(1)-C(5)-O(2)	175.(1)
Rh(1)-O(1)-C(3)	114.2(7)	C(5)-O(2)	1.16 (1)
C(2)-O(1)-C(3)	112.5(9)		

For the phenyl rings

Mean values**: C-C aryl 1.398 (4)

C-C-C aryl 119.96 (8)

P-C(1)aryl-C(2)aryl 119.4 (5)

For the anion

mean P(3)-F 1.57(1)

* Standard deviations in parenthesis.

** weighted means.

TABLE 4.2

$[RhL_1CO]^+ PF_6^-$

a) Distances of Atoms from various planes.*

Plane	Atoms	Distance	Weighted sums of squares**
1.	[P(1)]	0.034	0.004
	[P(2)]	0.036	
	[O(1)]	-0.037	
	[C(5)]	-0.033	
	Rh(1)	0.004	
2.	[P(1)]	0.033	0.005
	[P(2)]	0.035	
	[O(1)]	-0.038	
	[C(5)]	-0.034	
	[Rh(1)]	0.003	
3.	[P(1)]	0.042	0.010
	[P(2)]	0.047	
	[O(1)]	-0.060	
	[C(5)]	0.013	
	[O(2)]	-0.043	
	Rh(1)	0.019	
4.	[P(1)]		
	[O(1)]		
	[Rh(1)]		
	C(3)	-0.411	
	C(4)	0.013	
5.	[P(2)]		
	[O(1)]		
	[Rh(1)]		
	C(1)	0.225	
	C(2)	-0.259	

* Equations of the least squares planes are of the form AX+BY+CZ=D. Brackets enclose those atoms defining the planes and perpendicular distances from them are given in Å.

** The weighted sum of the squares of the distances of the component atoms from the computed least squares planes.

TABLE 4.2

b) Equations of the Planes of the form AX+BY+CZ=D

Plane	A	B	C	D
1.	0.2535	-0.8305	-0.4960	0.2712
2.	0.2535	-0.8306	-0.4959	0.2728
3.	0.2400	-0.8291	-0.5051	0.1189
4.	0.2566	-0.8396	-0.4787	0.2692
5.	0.2799	-0.8240	-0.4927	0.5858

Table 4.3 A comparison of some M-X bond lengths, where M=Rh or Ir, and X=P, C or O **

Compound	M-P	M-C	M-O	Coord. No.	Coord. geometry	Ref.
$(RhL_1CO)^+ PF_6^-$	2.307(3), 2.294(3)	1.78(1)	2.112(8)	4	Dist. squ. planar	*
$(RhL_2(CO)(MeOH))^+ PF_6^-$	2.343(4), 2.334(4)	1.75(2)	2.19(1)	4	Square planar	*
$(RhL_3(CO)(H_2O))^+ PF_6^-$	2.334(3), 2.343(3)	1.77(1)	2.107(6)	4	Dist. squ. planar	*
$Rh(PhP(-CH_2CH_2CH_2PPh_2)_2)(Cl)$	2.298(1), 2.201(2)			4	Square planar	2
$(Rh(dPe)_2)^+ ClO_4^-$	2.310(7), 2.313(6) 2.289(6), 2.310(6)			4	Square planar	1
$(Rh(O_2)(dPe)_2)^+ PF_6^-$	Mean 2.348(8)		2.026(8)	5	Trigonal bipyramidal	8
$Rh(SO_2)(Cl)(CO)(PPh_3)_2$	2.36(2), 2.36(2)	1.847(7)		5	Tetragonal pyramid	9
$Rh(CO)(H)(PPh_3)_3$	2.32, 2.32	1.83(3)		5	Trigonal bipyramidal	10
$(Ph_2AsCH_2AsPh_2)_2(Rh(CO)(Cl))_2$		1.80(1)		4	Square planar, bridged	4
$Rh(Cl)(PPh_3)_3$	2.329, 2.331 2.210(trans to Cl)			4	Squ. planar with tet. dist.	11
$Rh(CO)_2(acac)$		1.76(2) 1.75(2)	2.05(1) 2.06(1)	4	Square planar	12
$(Ir(dPe)_2(O_2))^+ PF_6^-$			1.98	5	Trigonal bipyramidal	8
$Ir(O_2)(CO)(Cl)(Ph_2EtP)_2$	2.37, 2.37	1.882	2.04 2.00	5	Trigonal bipyramidal	13

* This work.
**Standard deviations are in parenthesis.

cationic dPe complexes (Table 4.3). This could reflect a change in the σ/π bonding character of phosphorus due to the alkyl side chain substitutent,** the metal oxidation state, or a consequence of stereochemistry. The average Rh-P length in $[RhL_3CO(H_2O)]^+PF_6^-$ is normal (2.338(2)). The shortened rhodium-phosphorus bond length observed in $[RhL_1CO]^+ PF_6^-$ is therefore a direct consequence of the steric requirements of the ligand. By analogy the M-P bond lengths in cationic dPe complexes of rhodium and iridium are likely to be shorter for the same reason.

The Rh(1)-O(1) bond distance (2.112(8)) indicates a strong covalent interaction. There is no directly comparable X-ray data available for metal-ether bonds to either rhodium or iridium. The value is slightly longer than that observed in a nickel macrocyclic tetradentate imine-ether complex[3] and also slightly longer than that observed for a range of rhodium and iridium O_2 complexes, (Table 4.3). The comparable Rh-O bond in $[RhL_3CO(H_2O)]^+PF_6^-$ albeit from the oxygen of an hydrogen bonded water molecule is almost identical (2.107(6)). A very approximate value of a typical Rh-O bond length may be obtained by addition of the single bond covalent radii of Rh and O (0.66)*. An estimate of the Rh single bond covalent radius has been obtained by comparison of the lengths of a variety of Rh(I) and Ni(II) phosphorus and chlorine bonds, no attempt to correlate electronegativities has been made. The maximum range of (Rh-X) minus (Ni-X) is (-0.026 to 0.17) where X = P, Cl, or C. Taking the single bond covalent radius of Ni as 1.39* gives a value for Rh of 1.46 ± 0.10 Adding the covalent radius of oxygen (0.66) gives a range for Rh-O of 2.12 ± 0.10. It is perhaps fortuitous that the observed values for $[RhL_1CO]^+PF_6^-$ and $[RhL_3CO(H_2O)]^+PF_6^-$ (2.112(8), 2.107(6)) lie in this range, as do those of the rhodium and iridium dioxygen complexes already mentioned.

The Rh(1)-C(5) carbonyl bonding distance (1.78(1)) is compared with that of other CO complexes of rhodium and iridum (Table 4.3), these range from 1.70 - 2.08 Å indicating a slightly shortened bond. There is a small deviation from co-linearity for Rh(1)-C(5)-O(2) (175(1)) which cannot be explained in terms of non-bonded interactions or packing effects, similar small deviations have been observed previously.[4]

* Taken from Pauling: 'The Nature of the Chemical Bond'.

**This is unlikely since both dPe and Ph_3P are thought to be very similar in this respect. See ref. 32.

The Ligand

The ligand functions as a terdentate donor in contrast with the bidentate complexes formed in RhL_1ClCO*, and NiL_1Cl_2[5]. The bond angles and distances in both the phenyl rings and $-CH_2-CH_2-$ moietys of the chain are normal. There is a slight distortion from pure tetrahedral geometry for O(1), the angle between Rh(1)-O(1) and the plane C(2)-O(1)-C(3) is 39° and not 54.7° expected for pure tetrahedral geometry. There is a very significant distortion from tetrahedral geometry for P(1) and P(2) (Fig. 4.2). The Rh(1)-P-phenyl angles are increased whilst the Rh(1)-P-alkyl angles decrease, resulting in a proportional reduction of the C-P-C interbond angles. Similar although less marked distortions are observed in d^8 complexes of Rh and Ir[1], and arise from strain in the ring systems.

The dominant feature governing the structure of the bicyclic ring system is the staggered conformation about the C-C bonds. The exact conformation adopted after C-C torsion**[6] has been minimised results from a balance between torsion in the remaining bonds and phenyl group non-bonded interactions. The ligand binds assymetrically, torsion angles for the complex being shown in Figure 4.3 together with perspective views of the separated ring systems. In ring A C(3) lies 0.411 Å below the plane O(1)-Rh(1)-P(1)-C(4). Whilst in ring B C(2) and C(1) lie 0.259 Å below and 0.225 Å above the plane O(1)-Rh(1)-P(2), respectively. The torsion barrier about the Rh-P bonds must be low due to the eclipsed conformations observed, this is reasonable in view of the long bond distances involved which must reduce non-bonded interactions between substituents. Theoretical calculations of the conformational energies of five membered diamine chelate rings have been carried out by Gollogly and Hawkins[7]. The observed conformations of a range of d^8 complexes of transition metals[1] parallels this work. It was found that the energy term was strongly dependant upon the torsion angle, τ, about the CH_2-CH_2 bond and independent of τ(M-P). The same considerations appear to apply to the tridentate chelate studied here. Table 4.4 compared the torsion angles for five membered ring d^8 complexes*** with those for rings A & B of $[RhL_1CO]^+PF_6^-$. It is apparent that the values are very similar in both order and magnitude. The ligand therefore adopts a conformation energetically similar to that observed for d^8 complexes at the expense of considerable distortion to the metal co-ordination sphere.

*This work, Chapter 3. ** torsion as defined in ref.6. *** taken from ref.1 and updated from the literature.

Figure 4.2 Distortions from tetrahedral geometry at phosphorus due to the constraint of binding a seven membered chain at three co-planar sites about rhodium.

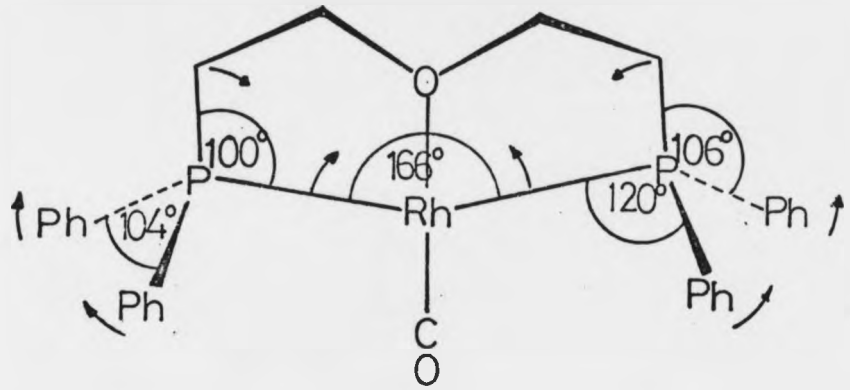
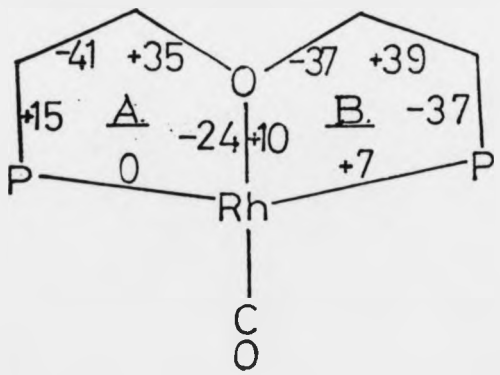


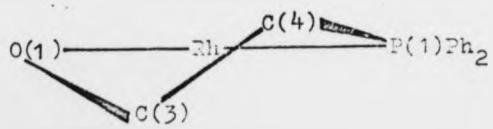
Figure 4.3 Torsion in the bi-cyclic ring system. Torsion values are written in the centre of the respective bonds inside the rings.

A. The fused ring system:



B. Conformations of the separate rings, viewed along the bisector of the P-Rh-O plane.

Ring A.



Ring B.

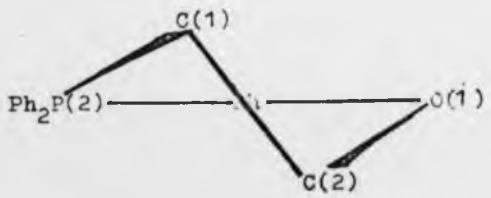


Table 4.4 Comparison of torsion angles for five membered chelate ring complexes.

Ref.	Compound	τ(M-L)	τ(P-C)	τ(C-C)	τ(C-P)	τ(P-M)
*	$(RhL_1CO)^+ PF_6^-$	-24	+35	-41	+15	0
		+10	-37	+39	-37	7
1	$(Rh(dPe)_2)^+ PF_6^-$	-32	+52	-43	+18	+10
		+26	-51	+51	-31	0
8	$(Rh(O_2)(dPe)_2)^+ PF_6^-$	-29	+52	-49	+24	+6
		+27	-46	+43	-21	-6
1	$(Ir(dPe)_2)^+ PF_6^-$	+30	-49	+42	-18	-9
		-26	+50	-48	+25	+3
14	$(Ir(dPe)_2(CO))^+ PF_6^-$	-17	+45	-54	+38	-8
		+31	-47	+38	-13	-12
8	$(Ir(O_2)(dPe)_2)^+ PF_6^-$	-26	+49	-50	+28	+3
		+24	-50	+53	-30	0
15	$(Ir(C_8H_{12})(dPe)(CH_3)$			0 ‡		
16	$(NiBr(dPe)(CH_2{:}CMeCH_2))$	+31	-54	+48	-22	-8
17	$(Ni(PNP)Br_2)$	No coordinates given, may be similar to $(RhL_1CO)^+ PF_6^-$.				

PNP is the ligand $(Ph_2PCH_2CH_2)_2N$.

Inter- and Intramolecular distances and Packing

There are no short (<3.5Å) inter or intramolecular contacts in the structure. The similarity between the conformations of this system and those of a variety of four and five co-ordinate dPe complexes has been noted and this despite widely varying spacegroups and substituents. The conformations must therefore be almost entirely governed by intermolecular interactions and steric requirements of the ligands rather than any particular influence of the metal atom concerned or the crystal packing.

The molecular packing arrangement is shown projected along (100) onto the (011) plane (Fig.4.4). The molecules are stacked in approximate planes parallel to (110) and crystal packing is largely governed by the phenyl rings. The PF_6^- anions occupy vacant lattice sites and there are no interactions either with the cation or adjacent substituents.

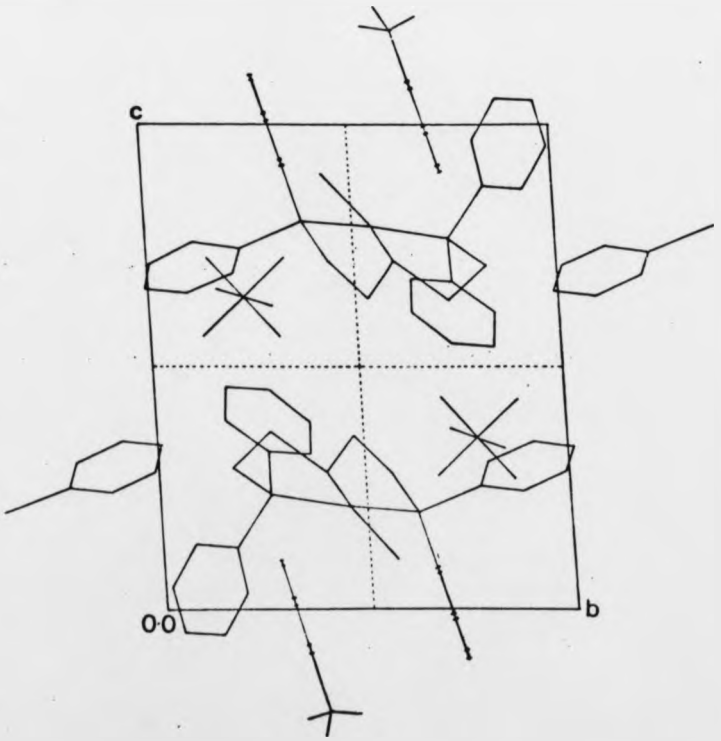


FIGURE 4.4

4.1.3. The crystal structure of $[RhL_3CO(H_2O)]^+PF_6^-$

The structure consists of discrete monomeric ions with an hydrogen bonded water molecule occupying one coordination site in the cation. A perspective view of the cation with labelling scheme is given in Fig. 4.5. Selected bond distances and angles are given in Table 4.5. Complete data on all measured and calculated parameters is given at the end of the chapter. The molecule has spacegroup $P\bar{1}$ with no imposed symmetry. Evidence of disorder was found in the -C(4)-O(2)-C(5)- portion of the chelate chain and data regarding these atoms is unreliable.*

Geometry about the metal.

The geometry of the coordination polyhedron about rhodium is very close to square planar. The Rh atom lies only 0.029 Å above the plane defined by P(1)-P(2)-O(5)-C(9) Table 4.6. P(1) and P(2) are close to pure trans(P(1)-Rh-P(2) 174.3(1)). Such small deviations are frequently observed, and have little 'energy cost'.

The Rh-P(1) and Rh-P(2) bond lengths are normal and close to those observed for a variety of triphenylphosphine derivatives (Table 4.3). Both the Rh-O(5) and Rh-CO bond distances are identical (W.E.L.) with those observed for $[RhL_1CO]^+PF_6^-$. (Table 4.3). Since $[RhL_3CO(H_2O)]^+PF_6^-$ is not a strained system (see following discussion) these are representative values of trans ether and carbonyl bonds to square planar Rh(I).

The Ligand

The ligand functions as a bidentate donor. The fourth coordination site at the metal is occupied by a water molecule which is hydrogen bonded to O(1) and O(3) of the chelate chain. Assuming a linear hydrogen bond the separations of O(1)-O(5) and O(3)-O(5) (2.69(1) and 2.67(1) are of the expected magnitude.[18] O_5 is pyramidal whereas O_1 and O_3 appear to be essentially trigonal, sp^2 hybridised (C(2)-O(1)-C(3) 116(1); C(6)-O(3)-C(7) 113(1)) with the hydrogen bonded protons almost coplanar with the respective C-O-C groups (Table 4.7).

* see experimental.

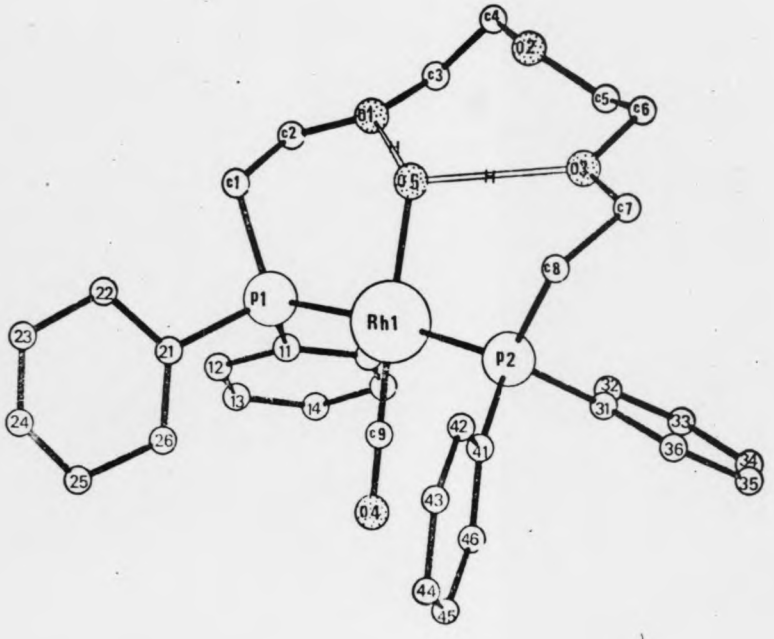


Figure 4.5 The Aquo(carbonyl)(bis1,11(diphenylphosphino)-3,6,9-trioxa-undecane) Rh(I) cation in crystals of its salt with hexafluorophosphate anion.

TABLE 4.5

$[RhL_3CO(H_2O)]^+PF_6^-$

Selected bond lengths (Å) and angles (°)*

about rhodium			
Rh(1) - P(1)	2.334(3)	P(1)-Rh(1)-P(2)	174.3(1)
Rh(1) - P(2)	2.343(2)	P(1)-Rh(1)-O(5)	92.1(2)
Rh(1) - O(5)	2.107(6)	P(1)-Rh(1)-C(9)	86.5(3)
Rh(1) - C(9)	1.77(1)	P(2)-Rh(1)-O(5)	93.1(2)
		P(2)-Rh(1)-C(9)	88.5(3)
		O(5)-Rh(1)-C(9)	173.7(5)
about phosphorus			
P(1) - C(11)	1.84(1)	Rh(1)-P(1)-C(11)	113.7(3)
P(1) - C(21)	1.82(1)	Rh(1)-P(1)-C(21)	112.1(3)
P(1) - C(1)	1.86(1)	Rh(1)-P(1)-C(1)	120.1(4)
P(2) - C(31)	1.82(1)	C(11)-P(1)-C(21)	105.1(5)
P(2) - C(41)	1.81(1)	C(11)-P(1)-C(1)	102.1(6)
P(2) - C(8)	1.86(1)	C(21)-P(1)-C(1)	102.0(5)
about oxygen			
O(5)-Rh(1)	2.107(6)	Rh(1)-O(5)-O(1)	103.7(3)
O(5)-O(3)	2.67(1)	Rh(1)-O(5)-O(3)	103.0(3)
O(5)-O(1)	2.69(1)	O(1)-O(5)-O(3)	111.4(3)
O(1)-C(2)	1.41(2)	C(2)-O(1)-C(3)	116.(1)
O(1)-C(3)	1.45(2)	C(2)-O(1)-O(5)	120.1(7)
		C(3)-O(1)-O(5)	123.6(8)
O(3)-C(6)	1.47(1)	C(6)-O(3)-C(7)	112 (1)
O(3)-C(7)	1.41(1)	C(6)-O(3)-O(5)	124.4(7)
O(4)-C(9)	1.15(1)	C(7)-O(3)-O(5)	123.3(6)
For the phenyl rings			
mean value**	C-C aryl	1.405(6)	
	C-C-C aryl	119.99(1)	
	P-C-C aryl	119.2(3)	
For the anion			
mean value**	P(3)-F	1.566(5)	

* Standard deviations in parenthesis

** Weighted means

TABLE 4.6

$(RhL_3CO(H_2O))^+ PF_6^-$

Distances of atoms from various planes*

a)

Plane	Atoms	Distance	Weighted Sum of squares**
1.	[P(1)	0.080	0.025
	P(2)	0.078	
	O(5)	-0.067	
	C(9)]	-0.090	
	Rh(1)	0.029	
2.	[P(1)	0.074	0.026
	P(2)	0.072	
	O(5)	-0.073	
	C(9)	-0.096	
	Rh(1)]	0.023	
3.	[C(2)		
	O(5)		
	C(3)]		
	O(1)	-0.073	

b) Equations of the planes of the form $Ax+By+Cz=D$

Plane	A	B	C	D
1.	-0.7533	-0.5377	-0.3787	-3.882
2.	-0.7533	-0.5377	-0.3787	-3.876
3.	0.8317	0.1248	-0.5410	-1.373

* Brackets enclose those atoms defining the planes, perpendicular distances from them are given in Å

** The weighted sum of the squares of the distances of the component atoms from the computed least squares planes.

Table 4.7. Geometry at Oxygen in $[RhL_3CO(H_2O)]^+PF_6^-$ measured by the angle of inclination of O----X to the Y-O-Z plane (tetrahedral = 54.7°).

O	°	X	Y	Z
O(1)	6°	O(5)	C(2)	C(3)
O(3)	9°	O(5)	C(6)	C(7)
O(5)	64°	Rh	O(1)	O(3)

The bond angles and distances in both the phenyl rings and $-CH_2-CH_2$ moietys of the chelate chain are normal.* The Rh-P-C angles are all significantly greater than tetrahedral, 109.47°, resulting in a proportionate reduction of the C-P-C interbond angles (Fig. 4.6).

The distortion observed at phosphorus together with the distortion from trans geometry tends to draw the chelate chain in towards the metal and optimises both the chain conformation and the Rh-O bond distance, exactly the reverse distortions are observed for $[RhL_1CO]^+PF_6^-$ in which the chelate chain is pushed back from the metal atom again optimising chain conformation and giving the same Rh-O bond distance.

The carbon atoms of the ethyl chains linking the phosphorus and oxygen atoms exhibit a gauche conformation (Table 4.8) models confirm the absence of any severe non-bonding interactions. Whilst it is possible to construct scale models having O(1), O(2) or O(3) donating directly to rhodium it is immediately obvious that these involve much less favourable chain conformations even allowing extensive distortion of the metal co-ordination sphere. This explains why water is so firmly bound in this complex: the binding site is geometrically almost perfect for accepting a hydrogen bonded water donor when the chelate chain is in an almost optimum conformation. Models also show a significant improvement in C-C torsion angles when O(1) and O(3) are sp^2 hybridised, this also results in the -C(3)-C(4)-O(2)-C(5)-C(6)- chain having two equal energy conformations with a very low torsion barrier between them and may explain the disorder observed in this region.

* allowing for disorder in -C(4)-O(2)-C(5)-

Figure 4.6 Distortions from tetrahedral geometry at phosphorus due to the constraint of binding a thirteen membered chain at three co-planar sites about rhodium. Compare figure 4.3 .

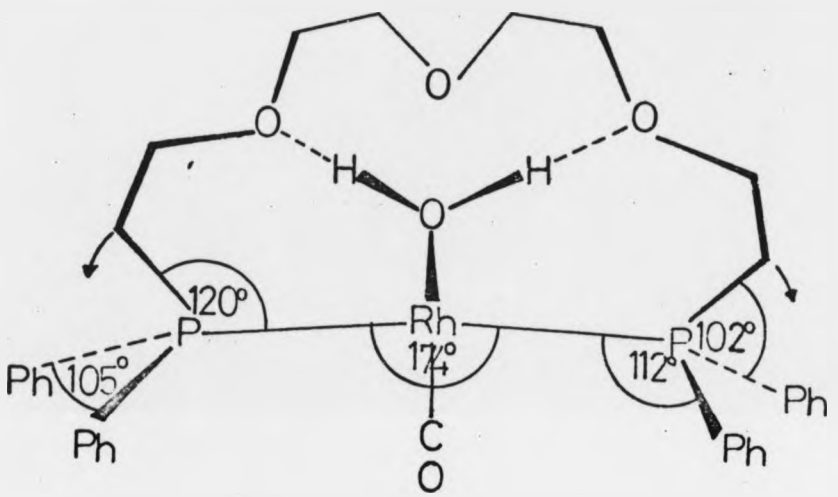


Table 4.8 Torsion angles for $[RhL_3CO(H_2O)]^+PF_6^-$

Defining Atoms	Value
Rh(1)-P(1)-C(1)-C(2)	-74
P(1)-C(1)-C(2)-O(1)	+69
O(1)-C(3)-C(4)-O(2)	+38
O(2)-C(5)-C(6)-O(3)	+61
O(3)-C(7)-C(8)-P(2)	-59
C(7)-C(8)-P(2)-Rh(1)	+86

Inter- and Intramolecular distances and packing

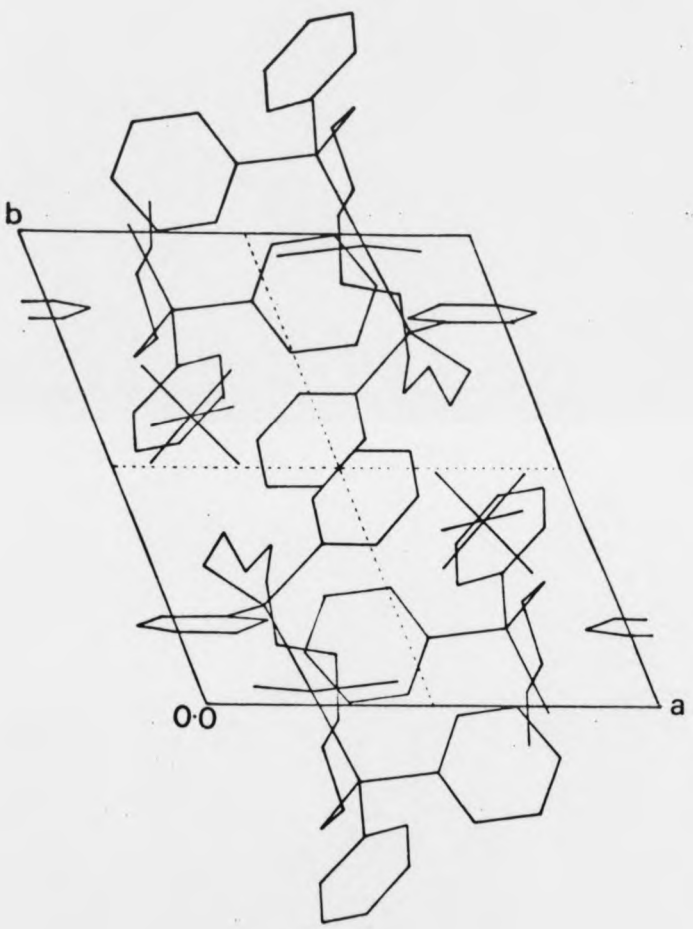
There are several short intramolecular contacts (Table 4.9). The Rh-H(26) and Rh-H(46) distances of ~3.0Å and the H(26)-H(46) separation of 2.7Å results in steric hinderance about a vacant axial coordination site.

The molecular packing arrangement is shown projected along (0, 0, 1) onto the (1, 1, 0) plane (Figure 4.8). The molecules are closely packed in planes parallel to (0, 1, 1).

Table 4.9 Nonbonded contact distances (< 3.8 Å) in $[RhL_3CO(H_2O)]^+PF_6^-$

Rh(1)-H(26)	2.97	H(36)-O(4)	2.61
Rh(1)-H(46)	3.04	Rh(1)-C(26)	3.55
H(26)-H(46)	2.70	Rh(1)-C(46)	3.60
H(12)-O(4)	2.64		

Figure 4.7 Packing Diagram for $(RhL_3CO(H_2O))^+ PF_6^-$.



4.1.4 The Crystal Structure of $\left[RhL_2CO(MeOH)\right]^+ PF_6^-$

The structure consists of discrete monomeric ions with a hydrogen bonded methanol molecule occupying one coordination site in the cation. A perspective view of the cation with labelling scheme is given in figure 4.8. Selected bond distances and angles are given in table 4.10. The structure has been refined to a current R value of 0.075. Tables of atomic coordinates and temperature factors are not included since further refinement is in progress. Disorder was found for the chelate chain and because of this bond distances and angles involving those atoms are unreliable.

Geometry about the Metal

The geometry of the coordination polyhedron about rhodium is close to square planar with P(1)-Rh-P(2) = 178.7(2) and O(1)-Rh-C(7) = 172.4(7). The Rh-P(1) and Rh-P(2) bond lengths are normal and identical (within one standard deviation) to those observed in $\left[RhL_3CO(H_2O)\right]^+ PF_6^-$, and similar to those observed for a variety of triphenylphosphine metal complexes (table 4.3). The Rh-CO bond length (1.75(2)) is normal but at the 3σ level of significance the Rh-O bond length (2.10(2)) appears very slightly longer than that observed in the analogous L_1 and L_3 complexes (table 4.3).

The Ligand

The ligand functions as a bidentate donor. The fourth coordination site at the metal is occupied by a MeOH molecule which is hydrogen bonded to O(4) of the chelate chain. It is significant that the major region of disorder in the chelate chain is at O(4), which was refined in two separate positions, O(4)(1) and O(4)(2), having site occupations of 70% and 30% respectively. Only O(4)(1) is within hydrogen bonding distance[18] of the MeOH hydrogen (O(4)(1)-O(1)(MeOH) = 2.64(2)) and it is probable that weak hydrogen bonding is responsible for the high site occupancy of O(4)(1). The assumption of a linear hydrogen bond between O(4)(1) and O(1) results in unreasonable hybridisation at O(1) (e.g. Rh-O(1)-O(4)(1) = 82.0(4)). It is thought that the MeOH hydrogen must lie off the line O(4)(1)-O(1), resulting in a non-linear hydrogen bond.

The angles at phosphorus (e.g. Rh-P(1)-C(1) = 114.0(6)) together with

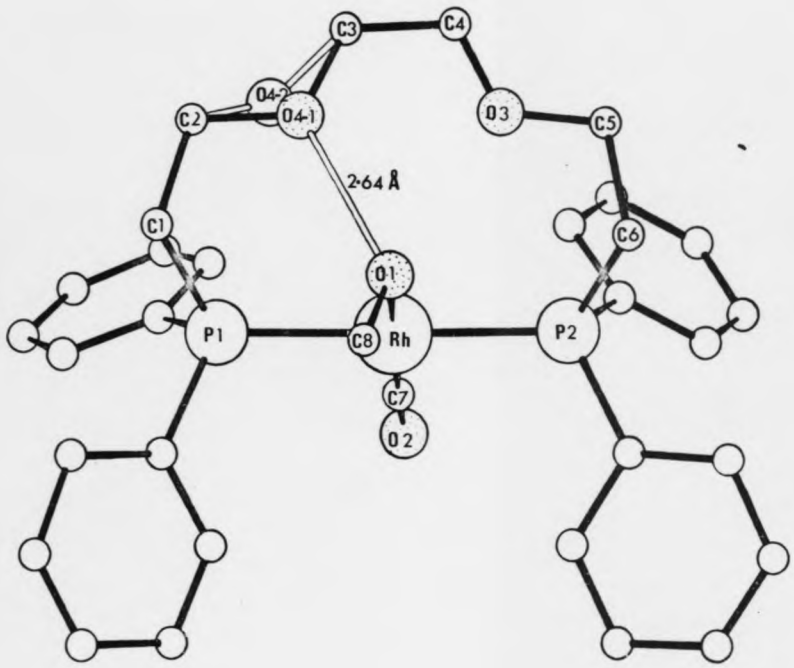


FIGURE 4.8

The [carbonyl][methanato][bis 1,8-(diphenylphosphino)-3,6-dioxa-octane] Rh(I) cation in crystals of its salt with hexafluorophosphate anion

TABLE 4.10

$[RhL_2CO(MeOH)]^+ PF_6^-$

Selected Bond Lengths (Å) and Angles (°) *

About rhodium			
Rh - P(1)	2.342(4)	P(1) - Rh - O(1)	89.6(3)
Rh - P(2)	2.334(4)	P(1) - Rh - C(7)	92.1(5)
Rh - O(1)	2.19(1)	P(2) - Rh - O(1)	90.6(3)
Rh - C(7)	1.75(2)	P(2) - Rh - C(7)	87.8(5)
P(1) - Rh - P(2)	178.7(2)	O(1) - Rh - C(7)	172.4(7)
About phosphorus			
P(1) - C(11)	1.85(2)	Rh - P(1) - C(11)	117.1(5)
P(1) - C(21)	1.83(2)	Rh - P(1) - C(21)	112.6(6)
P(1) - C(1)	1.87(2)	Rh - P(1) - C(1)	114.0(6)
P(2) - C(31)	1.81(2)	C(11) - P(1) - C(21)	104.1(7)
P(2) - C(41)	1.84(2)	C(11) - P(1) - C(1)	102.4(8)
P(2) - C(6)	1.88(2)	C(21) - P(1) - C(1)	105.2(8)
About oxygen			
O(1) - C(8)	1.46(2)	O(2) - C(7)	1.16(2)
O(1) - O(4)(1)	2.64(2)	Rh - O(1) - C(8)	124.9(9)
O(4)(1) - C(2)	1.48(2)	Rh - O(1) - O(4)(1)	82.0(4)
O(4)(1) - C(3)	1.40(2)	C(2) - O(4)(1) - C(3)	110(1)
O(4)(2) - C(2)	1.15(4)	C(2) - O(4)(1) - O(1)	121(1)
O(4)(2) - C(3)	1.38(4)	C(3) - O(4)(1) - O(1)	128(1)
O(3) - C(4)	1.31(2)	C(2) - O(4)(2) - C(3)	137(3)
O(3) - C(5)	1.40(2)	C(4) - O(3) - C(5)	121(1)
About carbon			
C(1) - C(2)	1.49(3)	O(4) - C(3) - C(4)	110(2)
C(3) - C(4)	1.49(3)	C(3) - C(4) - O(3)	112(2)
C(5) - C(6)	1.54(3)	O(3) - C(5) - C(6)	109(1)
P(1) - C(1) - C(2)	114(1)	C(5) - C(6) - P(2)	111(1)
C(1) - C(2) - O(4)	105(1)	Rh - C(7) - O(2)	179(1)
For the phenyl rings			
Mean values C - C aryl		1.40(3)	
C - C - C aryl		120(2)	
P - C - C aryl		120(1)	
For the anion			
Mean value of P(3) - F		1.54(2)	

* Standard deviations in parentheses

the P(1)-Rh-P(2) angle of 178.7(2), indicate that L_2 is of almost optimum size to act as a trans bidentate donor. This contrasts with L_1 and L_3 which are respectively too small and too large. At their closest approach O(4) and O(3) are only ca. 3.2Å from rhodium. Only small changes of ligand conformation are necessary to bring these atoms to within bonding distance of Rh. This supports the belief* that significant Rh-O (ligand) interaction occurs in solution and also explains why the MeOH free complex $[RhL_2CO]^+ PF_6^-$ is readily isolable.**

Since refinement of the positional and thermal parameters of the chelate chain is still in progress, the torsion angles about the $-CH_2-CH_2-$ bonds have not yet been calculated. However, perspective drawings indicate an essentially staggered conformation, as expected.

Crystal packing appears to be governed largely by the phenyl rings with the PF_6^- anions occupying vacant lattice sites.

A Comparison of the Structures of $[RhL_nCO(S)]^+ PF_6^-$ (where S = solvent or absent)

For the three complexes (9), (15) and (18) there is an approximately square planar arrangement of donor atoms about rhodium. In each case the principal distortion is an in plane deviation from square planarity. L_n (n = 1, 2 or 3) are required to be trans bidentate P-donors, since too much steric hindrance would arise if they functioned as cis-donors. The number of (CH_2CH_2O) groups between the phosphorus atoms is the only difference between the ligands. Therefore these ligands should have very similar σ and π-acceptor properties. The steric requirements of the three ligands will not be identical and this will also affect the disposition of the O-donors in the chain which may or may not be available for bonding to the metal. The change in steric requirements with increasing chain length is reflected by an increase in P-Rh-P,*** namely, 100.6(4) and 99.0(4) for L_1, 114.0(6) and 114.8(6) for L_2 and 120.1(4) and 118.4(4) for L_3. Despite the large angular changes at phosphorus and rhodium the angles between the phenyl rings remain remarkably constant,

* See section 3.3.2

** See section 3.3.2

*** The in-plane angle opposite to the carbon monoxide donor

and phenyl -P - phenyl varies by only ca. 3° for all members of the series. There is apparently much less flexibility in these angles than in the chelate ring. The net result of these angular changes is to move the phenyl rings towards the CO coordination site, thereby compensating for L_1 and L_3 being respectively too small and too big to bond undistorted trans. Qualitatively identical distortions have recently been reported[31] for the cis phosphorus ligands in the series $Pd(SCN)_2(\underset{\sim}{L}_n)$*, where $\underset{\sim}{L}_n = Ph_2P(CH_2)_nPPh_2$ and n = 1, 2 or 3. Furthermore, the increasing steric requirements of $\underset{\sim}{L}_n$ are thought to be responsible for a change in the mode of thiocyanate bonding from S,S when n = 1 to S,N for n = 2 and N,N with n = 3.

Conclusion

The structures of the cations $[RhL_n(CO)(S)]^+$ prove that L_n (n = 1, 2 or 3) are capable of functioning as either bidentate P or tridentate P and O-donors. This lends support for the belief that L_n may function as trans bidentate P-donors in the neutral precursors $RhL_n(Cl)(CO)$.

A private communication has been received from Dr. N. Alcock on the crystal structure of $RhL_1(Cl)(CO)$ which appears to have a dimeric phosphine bridged structure in the solid state. This contrasts with the solution molecular weight which was consistent with an extensively dissociated dimer. Presumably this behaviour reflects the inherent steric strain in forcing L_1 to act as a trans bidentate donor and as such would not be expected in the analogous L_2 and L_3 complexes.

The structure of $[RhL_1CO]^+ PF_6^-$ demonstrates that comparatively large distortions from square planar geometry at rhodium may be accommodated in order to minimise non-bonded interactions in the ligand chain. The importance of non-bonded interactions is further emphasised by the structure of $[RhL_3(CO)(H_2O)]^+ PF_6^-$ in which a hydrogen bonded H_2O molecule donates to the metal in preference to direct donation from O-donors of the ligand chain.

On the basis of this work it is clear that the addition of two $-CH_2-$ groups to L_1 to form the ligand $[(Ph_2P(CH_2)_3)_2O]$ would allow the formation of unstrained tridentate chelate complexes. This supports the belief that for bicyclic complexes (at least) six membered phosphorus chelate rings may be

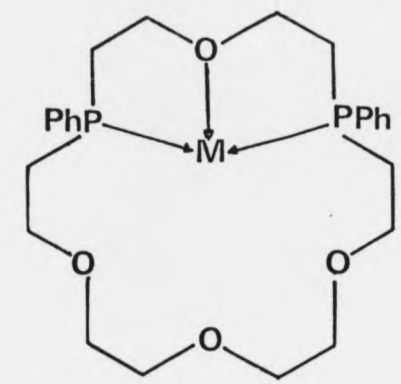
* Neither S nor N-bonding is implied

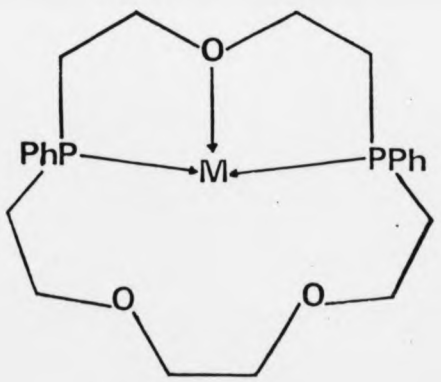
sterically more favourable than five membered rings.

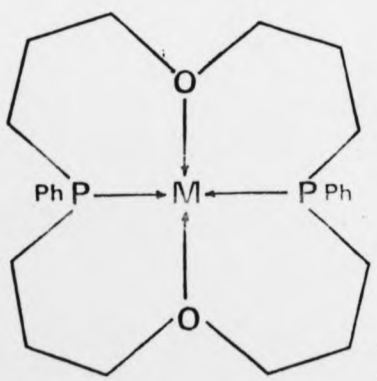
Since under suitable conditions O-donors of L_n can be made to co-ordinate to group VIII metals, it would be worthwhile investigating the analogous macrocyclic ligands in which the increased chelate effect might be expected to enhance such behaviour. Based on the structures of the linear systems, complexes of the type shown in Fig. 4.9 might be accessible. The ligand with propyl chains separating the donor atoms appears to be an ideal tetradentate donor and is particularly worthy of further study.

Figure 4.9

Some macrocyclic phosphino-ethers which might be worthy of further consideration.







Chapter 4.2 Experimental Section

4.2.1. Theoretical Considerations

A brief outline of the methods and parameters used to solve the structures is given. Detailed references may be obtained from standard texts.[19-22]

A. The Unit Cell and Lattice

Each molecule in a crystal is associated with a regular three dimensional point array, the lattice. This may be generated by the periodic repetition of three non-coplanar vectors, a, b and c with interaxial angles α, β and γ. These define the unit cell. An infinite number of sets of parallel planes, containing atoms, may be chosen from the lattice and specified by vectors (h k l) normal to them. An X-ray beam inpinging on a set of planes (h k l) at the Bragg angle will suffer diffraction and behave as if reflected - hence the common name "reflections".

B. The Structure Factor

X-rays are scattered by the bound electrons. The electron density $\rho(x\ y\ z)$ in the unit cell is a smooth periodic function over the whole lattice. Such functions may in general be expanded in terms of a Fourier Series. The Fourier expansion of the electron density function is:

$$\rho(x\ y\ z) = 1/V \sum_h \sum_k \sum_l F(hkl)\exp[-2\pi i(hx + ky + lz)] \qquad (1)$$

where F(hkl) is the coefficient to be determined, and h, k and l are integers over which the series is summed. This is known as the Structure Factor, and is a sum of the contributions of all atoms in reflection (hkl). It may be shown that

$$F(hkl) = \sum_j f_j \exp[2\pi i(hx + ky + lz)] \qquad (2)$$

where there are j atoms in the unit cell with phases ϕ given by:

$$\phi_j = 2\pi(hx + ky + lz) \qquad (3)$$

f is called the 'Atomic Scattering Factor' or 'Form Factor' and its value depends upon the type of atom and the Bragg angle θ. A scale is used such that f equals the number of electrons in the atom when $\theta = 0$.

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C. The Temperature Factor

Values of f must be corrected to allow for atomic vibration which has the effect of 'smearing' the electron density out over a greater volume in the unit cell. For a simple spherical or isotropic vibration:

$$f' = f \exp[-Bj(\mathrm{Sin}\Theta/\lambda)^2] \qquad (4)$$

more accurately a triaxial ellipsoidal anisotropic vibration may be assumed:

$$f' = f \exp[-\tfrac{1}{4}[h^2B_{11}(a^*)^2 + k^2B_{22}(b^*)^2 + l^2B_{33}(c^*)^2 + 2hkB_{12}a^*b^* + 2hlB_{13}a^*c^* + 2klB_{23}b^*c^*]] \qquad (5)$$

the values of B in both cases define the extent of atomic motion allowed in the crystal.

D. Relation of F(hkl) to Observable Intensities

The measured intensity of radiation reflected from plane (hkl) is proportional to $|F(hkl)|^2$. The magnitude of F(hkl) but not its phase may be determined experimentally. It is not therefore possible to compute the electron density distribution using equation (1) and solve the structure directly. There are various methods[23] of overcoming the phase problem. Only the heavy atom method[24-26] will be considered due to its appliciability to the compounds under study.

E. The Heavy Atom Method and Patterson Function

A. L. Patterson showed[24-26] that a Fourier Synthesis A(uvw) given by:

$$A(uvw) = \tfrac{1}{v} \sum_h \sum_k \sum_l [\,|F(hkl)|^2 \exp 2\pi i(hu + kv + lw)] \qquad (6)$$

is a map of all interatomic vectors in the unit cell. Unlike $\rho(x\ y\ z)$ this may be synthesised directly from observed $|F(hkl)|^2$ values. The peak heights are proportional to the atomic numbers of the atoms. If a unit cell contains N atoms there are (N^2-N) non origin vectors resulting in a very crowded and frequently intractable map. A molecule containing only a few heavy atoms will give a map dominated by heavy atom vectors.[27] In favourable cases these vectors may lead directly to the coordinates of the heavy atoms. The contribution of the f_j for the heavy atoms may dominate F(hkl). If this is the case an electron density synthesis using calculated values of F(hkl) based only on the heavy atoms should show the position of lighter atoms. The process may be iterated and if successful should rapidly converge to the final structure.

F. Least Squares Refinement

The refinement of a structure requires variation in the atomic parameters to be made such that a best fit is obtained between computed and observed structure factors. Legendres method of minimising the sum of the square of the errors is used to accomplish this. Both the theory and application of this method are well described in Standard texts.[20, 28]

Progress in structure refinement is frequently measured by the value of "The Residual, R", defined by:

$$R = \Sigma \left| |Fo| - |Fc| \right| / \Sigma |Fo| \qquad (7)$$

Wilson has shown[29] that an entirely wrong arrangement of atoms for a centric crystal has $R \approx 0.828$ correct structures have $R < 0.25$ and very well refined structures have $R \approx 0.05$.

G. Data Processing Corrections

Basic diffractometer intensity data must be corrected for effects which alter the observed value of F(hkl) from that calculated by first principles.[20]

(a). Background:† the Syntex $P2_1$ diffractometer measures a ninety-six step profile of each reflection with background counts on either side of the peak maximum. The corrected intensity I is given by

$$I = \text{(total scan count} - \frac{\text{sum of background counts)}}{\text{B.g. to scan ratio}} \times \text{scan rate}$$

$$\text{St. Deviation} = \text{(total scan count} - \frac{\text{sum of background counts)}}{\text{B.g. to scan ratio}}^{\frac{1}{2}} \times \text{scan rate}$$

(b). Coincidence correction:† the detector and associated circuity lose counts at high count rates due to inability to respond to a second pulse before the first pulse is processed. The true intensity may be approximated to the observed intensity by the Schiff formula,

$$It = Io \exp.(I_t \tau)$$

where τ is the dead time for an isolated event, and is an instrumental constant. The Syntex $P2_1$ approximates this expression by a parabola,

$$It = Io + \tau\, It^2$$

which fits well up to 50,000 cps.

† Syntex $P2_1$ manual.

(c) Polarization: the theory of polarisation effects is treated in Standard texts.[19, 20] The correction takes the form

$$|F(hkl)| \propto (I(hkl)/\rho)^{\frac{1}{2}}$$

where

$$\rho = \frac{(\cos^2 2\theta_m}{} \frac{\cos^2 \epsilon + \mathrm{Sin}^2 \phi \cos^2 2\theta + \cos^2 2\theta_m \mathrm{Sin}^2 \epsilon + \cos^2 \epsilon}{1 + \cos^2 2\theta_m}$$

where $2\theta_m$ is the Bragg angle of the monochromator and $\mathrm{Sin}\epsilon = \tan\mu \cot\theta$ and μ is the inclination angle.

(d) The Lorentz Factor: the time for a given reciprocal lattice point to travel through its diffraction position during data collection is not constant and is a function of data collection geometry. Since measured intensity is a function of scan rate a correction specific to the parallel geometry used in this determination is applied†

(e) Absorption: an X-ray beam travelling through a crystal is attenuated according to a normal exponential law,

$$I = Io \exp(-\mu\tau) \qquad (8)$$

where Io is the incident intensity, I the intensity after a distance τ and μ is the linear absorption coefficient of the crystal. μ depends upon the number and type of atoms in the given unit cell and is very dependant upon the wavelength of the radiation, (using Cu k_α radiation absorption corrections are often essential to enable satisfactory structure refinement). Application of equation (8) requires a full knowledge of the crystal dimensions referenced to the same coordinate set used for data collection. A measuring procedure and associated analytical absorption correction program due to Alcock[30] was used.

† Reference 20 Chapter 7.

4.2.2. Structure Determination and Experimental Data.

A. Structural determination was very similar for both complexes and only important differences are discussed in text.

Crystal Preparation and Mounting

The complexes, $[RhL_1CO]^+PF_6^-$ and $[RhL_3CO(H_2O)]^+PF_6^-$ were twice recrystallised from MeOH ($18^o \rightarrow -40^o$C) to yield pure microcrystalline material. Approximately 0.4 g of each was rapidly dissolved in hot MeOH (50^o) and cooled to room temperature over 5 minutes. Well developed yellow crystals in the form of narrow prisms and flat parallelopipeds were obtained in each case. Temperature control is critical, low temperature recrystallization afforded large agregates and decomposition occurs above 50^o giving a grey/green material of uncertain composition. Although slight decomposition is evident even at 50^o no difference whatsoever could be detected between the macro and microcrystalline materials.

For both complexes crystals of both shapes were selected. These were transparent, free of occlusions and had well developed faces, in addition they extinguished sharply under polarised light. The crystals were mounted on fine quartz fibres using "Kwikfill" polyester paste and subsequently mounted and alligned with the major prism axis in coincidence with the goniometer axis of rotation. As expected preliminary photographs showed no difference between the two major shapes of crystals observed for each complex. Further crystal data was collected from the prism shaped crystals.

Preliminary Unit Cell Data

Two 15^o oscillation photographs about the prism axis were recorded at setting 180^o appart using unfiltered Cu K_α radiation. Accurate alignment about a crystallographic axis was confirmed by the superimposition of layer lines. This axis was arbitrarily called c and the value of c was determined from the interplanar spacing.

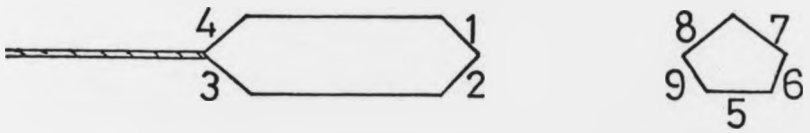
Zero, first and second layer equi-inclination Weissenberg photographs were recorded over 190^o using Ni filter Cu K_α radiation and 20 hour exposures. No systematic absences were detected and there was no axis of order greater than one. This indicates a triclinic lattice ($a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$) and space group $P\bar{1}$ was tentatively assigned to both crystals. Two arbitrary reciprocal lattice axes separated by γ^* (where γ^* was

chosen to be $\approx 90^{\circ}$) were selected and the layer spacing along them used to calculate a* and b*. The volumeof the primitive cell was calculated. The preliminary cell constants for both crystals were used as a guide only in the selection of the final unit cell vectors.

Crystal Dimensions

(a) $(RhL_1CO)^+PF_6^-$

Z mounting axis



The crystal was very regular (see figure) with 4 angular terminal faces and 5 prism faces. Using a microscope with a Vickers screw micrometer eyepiece and a Nonius crystal orienter measurements were made to determine the bounding faces of the crystal W.R.T. an orthogonal coordinate set using the method of Alcock.[30] The data was transposed to the diffractometer coordinate set and fitted to a set of plane equations of the type,

$$Ax + By + Cz = D$$

Values of A, B, C and D are tabulated in Table 4.11. Using the diffractometer orientation matrix calculated for the crystal (discussed under "Data collection") the planes were redefined in terms of their miller indices. These values were close to integer showing the crystal faces to be well developed crystallographic planes. Integer values were assumed and are also tabulated in Table 4.11. The five prism faces constitute a zone about (110).

(b) $[RhL_3CO(H_2O)]^+PF_6^-$

Mounting fibre

z axis

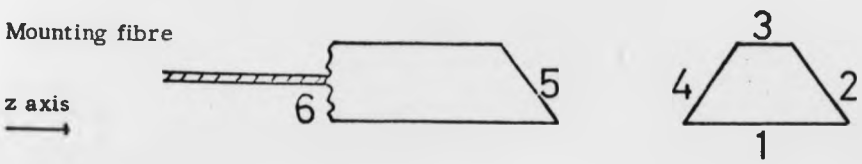


Table 4.11 Crystal Dimensions

$(RhL_1CO)^+ PF_6^-$

Plane	A	B	C	D	Miller Index
1	-0.643	+0.766	+1.705	0.00420	(0,1,0)
2	+0.788	-0.616	+0.882	0.01079	(1,0,0)
3	+0.719	-0.695	-1.834	0.00494	(0,-1,0)
4	-0.530	+0.848	-1.449	0.01835	(-1,0,0)
5	-0.829	+0.559	+0.160	0.01096	(-1,1,0)
6	0	+1.00	+0.045	0.00869	(-2,2,-3)
7	+0.995	-0.105	-0.123	0.00606	(1,-1,-1)
8	-0.052	-0.999	0.0	0.0450	(2,-2,3)
9	-0.985	+0.174	+0.184	0.0358	(-1,1,1)

$(RhL_3CO(H_2O))^+ PF_6^-$

Plane	A	B	C	D	Miller Index
1	+0.999	+0.0349	+0.164	0.003777	(-3,0,4)
2	-0.743	-0.669	-0.036	0.006357	(3,0,1)
3	-0.999	-0.349	-0.155	0.007604	(3,0,-4)
4	-0.629	+0.777	-0.139	0.006615	(0,0,-1)
5	-1.00	0.0	+0.575	0.004974	(4,-3,-3)
6	+0.951	+0.309	-2.840	0.021980	(-5,9,-2)

The crystal was regular with two angular terminal planes (6 damaged) and four prism faces. These were identified as 'D' planes and '(hkl)' planes as previously described. The four prism faces constitute a zone about (010) indicating that preliminary photographs had been taken about the b axis of the final cell. (Initially this axis was assigned as c). Plane data is in table 4.11.

Data Collection

Data were collected on a Syntex $P2_1$ 4-circle computer controlled diffractometer. Essential crystal data and instrumental conditions are tabulated in Tables 4.12 and 4.13. The position of fifteen strong reflections were automatically refined and the resultant data used in an autoindexing routine to generate a set of thirty possible interaxial vectors. No vector triples having more than triclinic symmetry were observed and three vectors were chosen to give the most nearly orthogonal cell having smallest volume. In both cases the chosen cells were similar to those obtained from initial rotation photographs and confirmed $P\bar{1}$ symmetry to be a reasonable choice. The data was subjected to least squares refinement and used to calculate an 'orientation matrix' and accurate unit cell parameters. The final matrix was used to control data collection, but in each case instability of the crystal W.R.T. the mounting fibre required two or more repetitions of this centering procedure, at different stages of data collection. Three reflections over a wide Sin Θ/λ range were selected and graphical intensity profiles were determined. These were smooth and well formed gaussian peaks. The peak width was used to determine the optimum scan width for data collection.

Data Processing

Computing was mainly with the programs of Dr. D. R. Russell on I.C.L. 4130 and 4120 computers. Basic diffractometer intensity data was processed and corrected as previously described. Atomic scattering factors and anomalous scattering factors (rhodium and phosphorus only) were from 'International Tables for Crystallography' Vol. 2. Reflections for which $I/I(\sigma)>3$ were considered observed, and used in structure determination. Tables of the final atomic coordinates, temperature factors and observed and calculated structure factors are included in section 4.2.2.C, at the end of the chapter.

Table 4.12 Basic Crystal Data.

	$(RhL_1CO)^+ PF_6^-$	$(RhL_3CO(H_2O))^+PF_6^-$
Molecular formula	$C_{29}H_{28}O_2F_6P_3Rh_1$	$C_{33}H_{38}O_5F_6P_3Rh_1$
Molecular weight	718	824
Cell dimensions:		
a	10.907 (3)	9.837 (2)
b	11.047 (2)	11.416 (2)
c	13.405 (3)	17.554 (3)
α	94.19 (2)	94.08 (2)
β	82.30 (2)	79.64 (1)
γ	107.98 (2)	111.98 (1)
Volume	1521.7 (6)	1798.3 (6)
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
d observed	1.61	-----
d calculated	1.57	1.52
Colour	golden yellow	pale yellow
Habit	prism developed along (110)	prism fragment prism axis (010)
Crystal dimensions	see Table 4.11	
Crystal volume	1.432×10^{-5}	0.523×10^{-5}
Absorption coefficient for MoKα	7.63 cm^{-1}	6.69 cm^{-1}
Range of transmission coefficients	0.89-0.96	0.96-0.97

Table 4.13 Diffractometer data collection details.

	$(RhL_1CO)^+ PF_6^-$	$(RhL_3CO(H_2O))^+ PF_6^-$
Radiation Monochromator	MoKα graphite crystal	MoKα graphite crystal
Scan speed	Variable 1.3-29.3, 2sec prescan	Variable 1.3-29.3 2sec prescan
Method	θ-2θ scans	
Scan width	Variable in the range $-0.5(\alpha_1)$ to $+0.5(\alpha_2)$	Variable in the range $-0.7(\alpha_1)$ to $+0.7(\alpha_2)$
Background time	0.5 of scan	0.5 of scan
Standards	(-1,1,1) (-1,2,1) (2,3,-1) every 150 reflections	(1,-1,-1) (2,0,0) (4,0,-2) every 150 reflections
Max. deviation in standards before re-centering	2σ	2.5σ
2θ limit	50°	55°
(hkl) range	+h ±k ±l	+h ±k ±l
No. of unique data	3565	6359
Reflections $I>3(\sigma)I$	2389	3106
Ambient temperature	20°	20°
Orientation matrix: Components of a* OX OY OZ Components of b* OX OY OZ Components of c* OX OY OZ	 0.056918 -0.037490 0.069102 -0.028690 0.035724 0.083470 -0.055340 -0.057?0 0.003590	 -0.093190 -0.060220 -0.006630 -0.014150 -0.032700 -0.087490 0.038220 -0.042470 0.009410

Solution of Structures

$[RhL_1CO]^+ PF_6^-$

The position of the rhodium atom was determined from a 3D Patterson synthesis based upon 2389 independent reflections. Least square refinement gave R =0·43. A fourier synthesis based upon the Rh phase was carried out, all phosphorus and fluorine atoms were immediately located. The structure was refined by successive fourier and least squares calculations using isotropic temperature factors until all non-hydrogen atoms had been located and identified. The fluorine atoms of the PF_6^- moiety showed considerable instability w.r.t. both coordinates and temperature factors during the early stages of refinement. Large anisotropic thermal motion of such counter ions is frequently encountered, in many cases rigid groups with fluorines octahedrally tied to phosphorus at optimum bond distance are employed to overcome this problem. It was found simpler to heavily damp the calculated least squares shifts for the PF_6^- during the early stages of refinement and to remove this constraint and introduce anisotropic temperature factors at a later stage.

Absorption corrections were applied to the data and the temperature factors for all atoms were significantly improved. At this stage all atoms were made anisotropic and several cycles of refinement gave a final R of 0.51.

A difference fourier showed no obvious errors in the model although slight disorder was indicated for the PF_6^- moiety. The remaining electron density in the difference map was readily assigned to the hydrogen atoms. These were not included in further refinement although fixed contributions at known bond distances and angles should have improved the R factor. A single spurious peak was observed with intensity approcimately equivalent to three or four hydrogen atoms. This was neither within bonding distance of another atom nor could it be attributed to a hydrogen bonded solvent molecule having only partial site occupation. The maximum remaining background density apart from this peak was approximately ≤ 1 hydrogen atom. A weight range analysis showed reasonable agreement between $(|Fo| - |Fc|)^2$ as a function of Fo and $Sin\Theta/\lambda$. Some adjustment was indicated but no improvement was obtained by the adoption of statistical weights.

$[RhL_3CO(H_2O)]^+ PF_6^-$

A similar procedure was followed. The positions of both the rhodium and phosphorus atoms was determined from a 3D Patterson Synthesis based upon 3106 reflections. As

before an iteration of 3D-fourier and least squares calculations was used to identify all remaining non hydrogen atoms. The presence of a water molecule donating to rhodium and hydrogen bonded to the chain oxygens O(1) and O(3) caused initial confusion, correct identification of all atoms rapidly following this discovery.

Absorption corrections were applied to a sample of the data set, but were considered unneccessary in view of the very small change in transmission coefficients (0.96 - 0.97). A final R factor of 0.057 was obtained with all non-hydrogen atoms anisotropic.

A difference fourier showed residual positive and negative regions at the rhodium and phosphorus positions. This was not attributable to badly estimated anisotropic temperature factors and probably arose from absorption errors. Residual electron density was assigned to hydrogen atoms. A calculated fixed hydrogen atom contribution (assuming normal geometry of phenyl rings and tetrahedral carbon atoms) was included in refinement. Whilst the R factor fell by only 0.005, standard deviations on variables were improved and a new difference map showed that most of the hydrogen atoms had been correctly placed. The final difference map showed evidence of disorder in the PF_6^- anion which was not considered serious. The anisotropic temperature factors of the C(4)-O(2)-C(5) outermost portion of the chelate chain were high and the difference fourier showed considerable disorder in the region of C(4). Bond distance and angles in this portion of the chain are suspect. In particular the short C(3)-C(4) bond (1.37(3)) is attributable to the large temperature factor of C(4). An attempt to correct this error would have required assuming two partially occupied sites for the disordered atoms in the C(4)-O(2)-C(5) chain and subsequent refinement. Since the important features of this structure are very well refined it was not possible to justify the additional expenditure of computer time neccessary to undertake this correction.

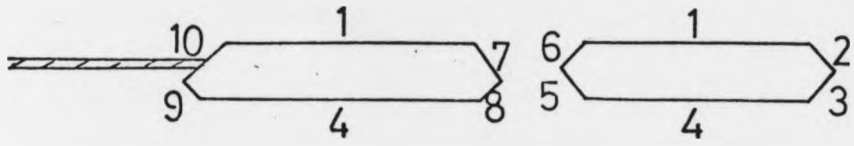
A similar weight range analysis to that obtained previously was derived and was not improved by statistical weighting.

B. Preliminary data and solution for $[RhL_2CO(MeOH)]^+PF_6^-$.

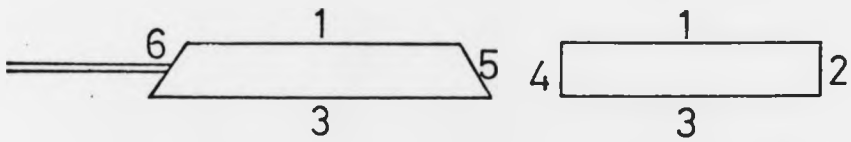
Crystal Preparation: The complex was recrystallised from MeOH(18 → -40°) to give pure microcrystalline material. This was recrystallised from hot MeOH(50°) and afforded well developed crystals as flat plates and parallelapipeds. Crystals were mounted and oriented as previously described.

Preliminary Cell Data : Oscillation and equi-inclination Weissenberg photographs indicated that the crystal had been mounted about the b axis of a monoclinic cell. The zero layer Weissenberg photographs showed absences of the type (hol), $l = 2n+1$ and spacegroup $P2_1/c$ was tentatively assigned. Suitable axes were selected from the zero level Weissenberg photograph and the volume of the unit cell was calculated. Preliminary cell data is tabulated in Table 4.14.

Crystal Dimensions.



The crystal was very regular with two pairs of angular terminal faces and six prism faces. To facilitate measurement and subsequent computation an approximate shape was assumed. On the basis of these measurements approximate faces (1-6) were identified as 'D' planes. (Table 4.14.)



Data were collected on a Syntex $P2_1$ diffractometer as previously described using CuK_α radiation. Essential crystal data and instrumental conditions are tabulated in Tables 4.14 and 4.15.

Solution of the Structure.

The position of the rhodium atom was determined from the 3D Patterson synthesis based upon 2374 independent reflections ($I/I\sigma > 3$). Least square refinement gave R =0.41. A fourier synthesis based upon the rhodium phase was carried out, two phosphorus, one oxygen and fragments of two phenyl rings were located. Iteration of this procedure resulted in the location of all non hydrogen atoms and gave R = 0.14 with isotropic temperature factors.

Absorption corrections were applied to the data set and four cycles of least squares refinement with the sequential introduction of anisotropic temperature factors for Rh, P, Fl and O gave R = 0.093. Disorder was observed in the chelate chain, principally at O(4) and to a lesser extent at O(3). O(4) was refined in two positions designated O(4)(1) and O(4)(2) with site occupations of 0.7 and 0.3 respectively. The disorder of the remaining atoms of the chain was reasonably approximated by large anisotropic temperature factors giving a final current R value of 0.075.

Bond distances and angles involving C(2)-O(4)(1)-C(3) are better than those of C(2)-O(4)(2)-C(3) since least squares refinement tends to favour the sites of highest occupation. A current difference fourier synthesis showed residual electron density in the region of O(3). Further refinement is progressing slowly since in a situation such as this where the disordered components of O(3) are separated by $\gtrsim 1$ Å it is difficult to refine both the positional and thermal parameters (particularly when using a diagonal least squares program). Finally it should be noted that bond distances of atoms with large anisotropic temperature factors appear artificially shortened. Accordingly, bond distances and angles in the chelate chain are subject to large errors. Final tables of temperature factors and atomic coordinates will be published when refinement is completed.

TABLE 4.14

Basic Crystal Data for $[RhL_2Co(MeOH)]^+ PF_6^-$

	Diffractometer	Photographs
Molecular formula	$C_{32}H_{36}O_4F_6P_3Rh_1$	
Molecular weight	794	
Cell dimensions:		
a	9.115(2)	9.1
b	16.790(5)	17.1
c	23.424(5)	23.6
α	89.98(2)	90
β	95.81(2)	94
ɣ	89.95(2)	90
Volume	3583(1)	3670
Spacegroup	$P2_1/c$	$P2_1/c$
Z	4	
d calculated	1.38	
Colour	Golden yellow	
Habit	Well developed prism	
Absences	(hol), l = 2n ; (oko), k = 2n	
Crystal dimensions	See Table 4.14	
Crystal volume	0.222×10^{-5}	
Absorption coefficient for CuKα	57.86 cm^{-1}	
Range of calculated transmission coefficients	0.64 - 0.86	

Crystal Dimensions for $[RhL_2CO(MeOH)]^+ PF_6^-$

Plane	A	B	C	D	Miller Index
1	0.985	-0.174	0.173	0.00141	(0, 0, 1)
2	-0.292	-0.956	0.059	0.00687	(-5, 1, 0)*
3	-0.988	0.156	-0.02	0.00469	(0, 0, -1)
4	0.292	0.956	0.098	0.00828	(10, 1, 1)*
5	0.985	-0.174	0.466	0.00148	(0, 1, 4)*
6	0.985	-1.174	-2.145	0.03060	(0, -2, 1)*

* Approximate planes - see text

Table 4.15 Diffractometer Data Collection Details for $(RhL_2CO(MeOH))^+ PF_6^-$.

Radiation	CuKα
Monochromator	Graphite crystal
Scan speed	Variable 3-29.3 depending upon an 8 sec prescan. Peaks for which $I/I(\sigma)<3$ were not collected.
Method	0-20 scans
Scan width	Variable in the range $-1.2(\alpha_1)$ to $+0.9(\alpha_2)$
Standards	(0,4,-1), (2,0,2), (1,0,2) collected every 100 reflections
2θ limit	120°
Max. (hkl) range	(0,0,-28) to (15,28,28)
No. of unique data	2700
No. data with $I>3\sigma I$	2374
Ambient temperature	20°
Orientation matrix:	
Components of a*	
OX	0.02978
OY	0.10565
OZ	0.00428
Components of b*	
OX	-0.00562
OY	-0.00081
OZ	0.05920
Components of c*	
OX	0.04208
OY	-0.00746
OZ	0.00390

Table 4.16 Atomic coordinates ($\times 10^4$) for $(RhL_1CO)^+ PF_6^-$*

Atom	X	Y	Z
Rh	11140 (1)	4533 (1)	2089 (1)
P(1)	13059 (3)	6181 (3)	2004 (3)
P(2)	9523 (3)	2642 (3)	2345 (2)
P(3)	2210 (3)	2285 (4)	6478 (3)
F(1)	1210 (9)	2984 (9)	6307 (9)
F(2)	3175 (9)	3124 (10)	5626 (8)
F(3)	2776 (11)	3330 (11)	7271 (8)
F(4)	1642 (11)	1259 (10)	5661 (8)
F(5)	1236 (10)	1417 (10)	7268 (8)
F(6)	3248 (9)	1642 (10)	6637 (9)
O(1)	12099 (8)	3750 (8)	3018 (7)
O(2)	9597 (10)	5616 (10)	986 (8)
C(21)	14085 (11)	6527 (11)	803 (10)
C(22)	15393 (13)	6547 (13)	703 (11)
C(23)	16111 (13)	6855 (13)	-298 (11)
C(24)	15561 (15)	7104 (14)	-1054 (12)
C(25)	14251 (16)	7064 (16)	-933 (12)
C(26)	13528 (15)	6791 (15)	10 (11)
C(11)	13061 (10)	7741 (11)	2534 (9)
C(12)	11899 (11)	7900 (12)	3014 (10)
C(13)	11907 (13)	9087 (14)	3483 (11)
C(14)	13076 (13)	10117 (13)	3404 (11)
C(15)	14200 (13)	9939 (13)	2911 (11)
C(16)	14232 (12)	8743 (12)	2480 (10)
C(31)	8114 (12)	2643 (11)	3251 (9)
C(32)	7551 (13)	1665 (14)	3912 (10)
C(33)	6418 (14)	1736 (16)	4601 (11)
C(34)	5904 (14)	2722 (15)	4519 (11)
C(35)	6468 (15)	3669 (15)	3862 (13)
C(36)	7622 (12)	3668 (13)	3214 (10)
C(41)	8914 (11)	1704 (11)	1258 (9)
C(42)	9636 (13)	1910 (13)	344 (11)
C(43)	9210 (14)	1229 (14)	-531 (11)
C(44)	7995 (15)	354 (14)	-480 (12)
C(45)	7220 (16)	114 (15)	431 (12)
C(46)	7688 (14)	775 (13)	1318 (11)
C(1)	10432 (12)	1762 (12)	2930 (10)
C(2)	11292 (13)	2685 (13)	3642 (11)
C(3)	13052 (13)	4711 (13)	3586 (10)
C(4)	13993 (12)	5573 (13)	2793 (10)
C(5)	10247 (12)	5195 (12)	1385 (10)

* Fractional coordinates, with standard deviations in parentheses.

Table 4.17 Anisotropic Temperature Factors (x10) for $(RhL_1CO)^+ PF_6^-$.

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rh	28(0.4)	29(0.4)	36(0.5)	5(0.3)	-5(0.3)	4(0.3)
P(1)	28(1)	32(2)	38(2)	-2(1)	-3(1)	6(1)
P(2)	34(1)	29(2)	37(2)	7(1)	-1(1)	7(1)
P(3)	34(2)	57(2)	46(2)	6(2)	1(1)	1(1)
F(1)	49(5)	97(7)	144(8)	-3(6)	-13(5)	39(5)
F(2)	74(6)	107(7)	105(7)	47(6)	29(5)	37(5)
F(3)	99(7)	99(7)	95(7)	-20(6)	-40(6)	8(6)
F(4)	131(8)	83(7)	83(7)	-24(5)	-27(6)	36(6)
F(5)	87(6)	110(8)	86(7)	31(6)	14(5)	-1(5)
F(6)	72(6)	114(8)	155(9)	53(7)	-10(6)	50(6)
O(1)	34(4)	45(5)	50(5)	6(4)	-9(3)	11(3)
O(2)	67(6)	65(6)	64(6)	10(5)	-14(5)	26(5)
C(21)	40(6)	19(5)	44(7)	-4(5)	3(5)	5(5)
C(22)	38(6)	38(7)	68(9)	6(6)	8(6)	3(5)
C(23)	46(7)	44(7)	72(9)	2(6)	17(6)	12(5)
C(24)	72(9)	47(8)	58(9)	-12(7)	8(7)	13(7)
C(25)	74(10)	77(10)	57(10)	5(8)	3(7)	21(8)
C(26)	71(9)	62(9)	47(8)	10(7)	-3(6)	21(7)
C(11)	30(5)	35(5)	32(6)	0.1(5)	-3(4)	9(4)
C(12)	34(5)	47(7)	50(7)	-1(6)	-5(5)	18(5)
C(13)	47(7)	58(8)	59(9)	-2(6)	-8(6)	22(6)
C(14)	55(7)	36(7)	64(8)	-0.1(6)	-6(6)	15(6)
C(15)	40(7)	39(7)	57(8)	-5(6)	-9(6)	11(5)
C(16)	36(6)	39(6)	46(7)	-11(5)	-3(5)	3(5)
C(31)	38(6)	34(6)	36(6)	-3(5)	-5(5)	5(5)
C(32)	47(7)	62(8)	36(7)	9(6)	-0.3(6)	5(6)
C(33)	55(8)	36(10)	37(8)	4(7)	-2(6)	4(7)
C(34)	56(8)	75(9)	42(7)	-14(7)	-3(6)	13(7)
C(35)	49(8)	67(9)	78(10)	-22(8)	-7(7)	14(7)
C(36)	39(6)	48(7)	44(8)	0(6)	3(5)	11(5)
C(41)	34(5)	24(5)	40(6)	7(4)	2(4)	6(4)
C(42)	56(7)	38(7)	52(8)	-1(6)	-4(6)	12(6)
C(43)	64(8)	51(8)	50(8)	-1(7)	2(6)	12(6)
C(44)	74(9)	43(8)	47(9)	-6(7)	-4(7)	6(7)
C(45)	72(9)	56(9)	50(8)	-14(7)	3(7)	-8(7)
C(46)	58(8)	36(7)	56(8)	-8(6)	3(6)	-4(6)
C(1)	45(6)	25(6)	62(8)	18(5)	-13(5)	11(5)
C(2)	46(7)	54(7)	56(8)	27(6)	-12(6)	9(6)
C(3)	47(7)	59(8)	48(8)	10(6)	-25(6)	-4(6)
C(4)	34(5)	47(7)	48(7)	12(5)	-15(5)	6(5)
C(5)	40(6)	37(6)	48(7)	6(5)	-7(5)	4(5)

Table 4.18 Atomic coordinates* (10^4) for $RhL_3CO(H_2O)^+PF_6^-$.

Atom	X	Y	Z
Rh(1)	2395(1)	313(0.8)	2245(0.5)
P(1)	2167(3)	2144(3)	1872(1)
P(2)	2662(3)	-1575(2)	2489(2)
P(3)	7723(4)	3921(3)	3844(2)
F(1)	6735(10)	3686(9)	4665(4)
F(2)	8735(9)	4172(8)	3021(4)
F(3)	7151(13)	4966(9)	3685(6)
F(4)	9026(11)	4913(8)	4202(6)
F(5)	6445(11)	2946(9)	3458(5)
F(6)	8341(10)	2872(7)	3975(5)
O(1)	2044(11)	2827(8)	3715(6)
O(2)	2106(14)	1349(11)	4906(6)
O(3)	2179(10)	-863(7)	4224(4)
O(4)	4413(13)	517(8)	772(5)
C(11)	1251(14)	1924(10)	1016(8)
C(12)	2070(16)	1792(11)	300(7)
C(13)	1354(19)	1610(12)	-401(9)
C(14)	-80(17)	1578(11)	-260(9)
C(15)	-924(19)	1680(13)	437(11)
C(16)	-255(17)	1874(12)	1134(10)
C(21)	3969(11)	3407(9)	1609(6)
C(22)	4133(13)	4408(9)	1147(6)
C(23)	5530(13)	5409(9)	1015(6)
C(24)	6696(12)	5398(9)	1337(6)
C(25)	6510(13)	4402(10)	1821(6)
C(26)	5126(13)	3405(10)	1950(6)
C(31)	2293(11)	-2687(8)	1687(6)
C(32)	936(12)	3705(9)	1731(6)
C(33)	643(13)	-4551(10)	1104(7)
C(34)	1673(13)	-4346(10)	423(6)
C(35)	3032(13)	3320(9)	375(6)
C(36)	3329(12)	-2501(9)	1010(6)
C(41)	4526(12)	-1376(10)	2617(6)
C(42)	4951(14)	-2428(11)	2597(7)
C(43)	6405(18)	-2239(14)	2738(8)
C(44)	7364(16)	-1013(14)	2893(8)
C(45)	6915(15)	11(12)	2926(8)
C(46)	5500(13)	-160(10)	2789(6)
C(1)	1142(14)	2960(11)	2566(7)
C(2)	1946(16)	3684(11)	3205(8)
C(3)	2813(21)	3383(14)	4360(9)
C(4)	2410(29)	2632(19)	4999(12)
C(5)	3283(19)	1001(14)	4933(10)
C(6)	2773(21)	-356(14)	4939(9)
C(7)	2031(16)	-2131(10)	4100(6)
C(8)	1423(14)	-2550(10)	3324(6)
C(9)	3596(16)	413(10)	1352(7)
O(5)	1173(8)	356(6)	3356(3)

*Fractional coordinates, with standard deviations in parenthesis.

Table 4.19 Anisotropic Temperature Factors (x10) for $RhL_3CO(H_2O)^+ PF_6^-$.

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rh(1)	39(0.4)	30(0.3)	34(0.4)	3(0.2)	-4(0.3)	13(0.3)
P(2)	44(2)	34(1)	50(1)	6(1)	-11(1)	14(1)
P(2)	46(2)	28(1)	34(1)	3(1)	-7(1)	12(1)
P(3)	56(2)	50(2)	48(2)	-1(1)	-6(1)	18(1)
F(1)	87(6)	137(7)	51(4)	-2(4)	4(4)	34(5)
F(2)	80(5)	114(6)	64(4)	32(4)	12(4)	54(4)
F(3)	160(9)	109(6)	123(7)	-9(5)	-31(6)	98(6)
F(4)	85(6)	85(5)	124(7)	-7(5)	-38(5)	-1(4)
F(5)	90(6)	104(6)	81(5)	-20(4)	-28(5)	4(5)
F(6)	121(6)	79(5)	75(4)	18(4)	-12(4)	53(5)
O(1)	89(6)	58(5)	93(6)	-27(4)	-36(5)	35(5)
O(2)	140(10)	103(7)	94(7)	-51(6)	-50(7)	56(7)
O(3)	96(6)	54(4)	39(4)	0.2(3)	-23(4)	23(4)
O(4)	140(8)	63(5)	65(5)	24(4)	44(5)	54(5)
C(11)	64(7)	30(5)	80(8)	13(5)	-25(6)	9(5)
C(12)	95(9)	38(5)	60(7)	11(5)	-35(7)	2(7)
C(13)	121(12)	39(6)	95(10)	30(6)	-46(9)	-5(7)
C(14)	98(10)	39(6)	109(10)	27(6)	-46(8)	-5(6)
C(15)	100(12)	52(7)	162(14)	30(8)	-75(10)	4(7)
C(16)	77(9)	50(7)	135(11)	26(7)	-58(8)	12(6)
C(21)	39(5)	31(4)	39(5)	5(3)	-5(4)	13(4)
C(22)	57(6)	30(4)	47(5)	1(4)	-12(5)	19(4)
C(23)	59(7)	35(5)	51(6)	-4(4)	-10(5)	19(5)
C(24)	41(6)	39(5)	46(5)	2(4)	-4(4)	11(4)
C(25)	46(6)	47(5)	44(5)	2(4)	-16(5)	10(5)
C(26)	50(6)	42(5)	46(5)	8(4)	5(5)	19(5)
C(31)	40(5)	23(4)	41(5)	4(3)	-6(4)	11(4)
C(32)	42(6)	32(5)	50(6)	3(4)	-10(4)	11(4)
C(33)	42(6)	47(5)	57(6)	-5(4)	-17(5)	20(5)
C(34)	53(6)	51(6)	53(6)	-10(4)	-27(5)	28(5)
C(35)	50(6)	40(5)	51(5)	-7(4)	-18(5)	21(5)
C(36)	50(6)	39(5)	36(5)	5(4)	-10(4)	24(4)
C(41)	44(6)	46(5)	33(5)	0.3(4)	-10(4)	14(4)
C(42)	64(8)	57(6)	69(7)	-12(5)	-27(6)	35(6)
C(43)	102(10)	97(9)	63(7)	-30(7)	-39(7)	65(8)
C(44)	59(8)	103(10)	66(8)	-18(7)	-20(7)	27(7)
C(45)	60(8)	66(7)	62(7)	-9(6)	-19(6)	9(6)
C(46)	50(7)	52(6)	47(6)	1(5)	-24(5)	1(5)
C(1)	51(7)	55(6)	76(7)	-2(5)	-4(6)	33(5)
C(2)	83(9)	46(6)	73(7)	-12(5)	-8(7)	31(6)
C(3)	146(15)	67(8)	63(8)	-29(7)	-23(9)	5(9)
C(4)	[illegible]	119(13)	117(14)	-29(11)	[illegible]	[illegible]
C(5)	110(12)	72(8)	102(10)	-28(8)	-47(9)	40(8)
C(6)	144(14)	74(8)	70(8)	-1(7)	-71(9)	[illegible]
C(7)	93(9)	40(5)	38(5)	4(4)	-21(6)	[illegible]
C(8)	69(7)	40(5)	33(5)	12(4)	-6(5)	6(5)
C(9)	103(10)	34(5)	58(7)	14(5)	8(6)	35(6)
O(5)	43(4)	44(3)	38(3)	-1(3)	2(3)	15(3)

Standard deviations in parenthesis.

TABLE 4.20 STRUCTURE FACTORS for $(RhL_1CO)^+ PF_6^-$

* H=	0	K= 0	-2	460	438	-11	186	188	0	163	175
2	454	477	-1	299	305	-10	240	241	1	240	266
3	149	161	0	130	154	-9	364	363	2	312	315
4	192	162	1	327	303	-8	181	187	3	131	136
5	117	141	2	880	859	-7	379	387	4	280	282
6	211	192	3	147	152	-6	83	71	6	222	221
7	264	259	6	315	325	-5	276	273	8	201	216
8	172	176	7	270	257	-4	124	116	9	81	80
9	86	61	8	244	244	-3	269	266	10	226	237
10	66	63	9	286	302	-2	332	329	11	78	98
11	146	157	10	79	73	-1	363	379	12	106	97
15	105	96	11	272	283	0	308	302	13	63	62
* H=	0	K= 1	12	90	100	1	315	301	* H=	0	K= 7
-20	76	79	13	212	216	2	321	312	-17	93	80
-18	99	80	14	152	146	3	119	109	-12	81	80
-16	70	81	15	158	168	4	65	59	-11	94	86
-15	64	60	17	91	104	5	81	82	-10	97	96
-14	177	192	18	73	75	6	228	236	-2	68	55
-11	75	72	* H=	0	K= 3	7	59	42	-1	257	273
-10	102	109	-20	81	73	8	238	226	0	66	70
-9	133	142	-16	133	126	10	106	117	1	219	225
-8	85	91	-17	69	62	12	91	99	2	194	192
-7	167	162	-16	138	129	15	88	91	3	238	239
-6	46	52	-14	221	237	16	67	80	4	223	225
-5	274	260	-13	166	168	17	88	99	5	136	139
-4	541	548	-12	259	255	* H=	0	K= 5	6	151	148
-3	118	121	-11	112	107	-18	79	80	8	286	294
-2	506	519	-10	73	100	-12	201	194	9	83	55
-1	334	359	-9	123	141	-11	87	88	10	206	199
0	311	307	-8	259	250	-10	210	204	13	71	65
1	202	163	-7	245	260	-9	113	127	15	111	108
2	246	272	-6	96	93	-8	149	148	17	73	70
3	399	411	-5	202	202	-7	235	216	* H=	0	K= 8
4	1072	1045	-4	98	80	-6	225	242	-15	101	104
5	227	248	-3	216	222	-5	265	265	-14	78	70
6	429	411	-2	480	416	-4	65	67	-13	73	63
7	415	396	0	184	181	-3	396	400	-12	129	131
8	282	289	1	566	502	-2	162	170	-11	71	84
9	267	278	2	345	329	-1	503	482	-10	161	155
11	383	388	3	79	96	0	250	257	-8	113	119
12	113	118	4	124	98	1	96	77	-7	133	132
13	143	140	5	125	106	2	320	310	-6	129	123
14	121	128	6	63	43	3	256	256	-5	62	68
16	117	114	7	187	178	4	227	247	-2	105	103
* H=	0	K= 2	8	113	109	5	71	70	1	256	267
-20	75	87	9	120	137	6	317	327	6	94	92
-18	120	115	10	86	83	8	125	127	7	128	121
-16	114	123	11	134	181	13	100	106	8	145	134
-14	192	200	12	78	76	14	97	92	9	80	70
-13	99	109	13	180	190	* H=	0	K= 6	10	116	117
-12	155	153	15	90	93	-12	101	105	12	127	124
-11	219	223	16	130	124	-9	108	100	13	97	101
-10	180	180	17	92	88	-8	131	136	* H=	0	K= 9
-9	237	240	18	94	103	-7	90	95	-13	139	141
-8	135	148	19	77	74	-6	83	77	-12	148	137
-7	56	58	* H=	0	K= 4	-5	203	208	-10	175	185
-6	48	63	-18	87	89	-4	127	127	-8	190	196
-5	116	103	-16	104	98	-3	132	142	-6	184	173
-4	150	157	-14	147	152	-2	157	152	-4	130	134
-3	116	100	-12	179	170	-1	474	477	-3	175	188

-1	84	83	0	228	231	-1	59	82	15	70	62
0	67	70	1	144	147	0	333	324	* H= 1 K= -4		
4	81	76	2	219	228	1	86	81	-14	103	110
5	124	119	3	251	247	2	133	143	-13	64	86
10	73	73	5	157	164	5	81	89	-12	97	89
* H= 0 K= 10			6	67	60	6	89	91	-10	60	58
-10	127	134	7	145	142	8	84	79	-9	96	94
-9	74	68	9	130	130	11	116	126	-8	120	106
-8	147	133	13	72	73	12	63	46	-7	199	207
-6	105	104	* H= 1 K= -9			13	165	159	-5	158	174
-4	197	199	-11	89	78	16	112	106	-4	49	50
-3	92	99	-7	64	45	* H= 1 K= -6			-3	110	128
-2	167	165	-3	111	112	-14	88	87	-2	87	98
-1	68	77	-2	111	95	-12	70	64	-1	138	129
0	97	104	-1	73	74	-11	112	121	0	263	272
1	221	234	2	88	100	-9	311	307	1	553	525
3	165	170	3	181	199	-8	61	51	2	636	622
8	66	64	4	112	110	-7	243	263	3	54	23
* H= 0 K= 11			5	165	161	-6	60	67	4	310	332
-6	133	133	6	147	148	-5	317	331	5	208	194
-4	99	99	7	174	178	-4	76	81	6	325	342
-2	77	79	9	194	190	-3	255	257	7	189	194
-1	163	164	11	218	215	-2	253	245	8	352	354
1	120	130	12	71	73	-1	353	352	9	258	277
3	89	98	13	120	112	0	333	340	10	114	115
5	139	133	14	136	129	1	157	140	11	262	269
7	87	102	* H= 1 K= -8			2	283	297	12	131	133
* H= 0 K= 12			-14	94	78	3	81	81	13	214	225
-2	101	97	-13	84	66	4	271	269	15	70	78
0	74	63	-11	159	164	6	184	188	17	90	86
1	72	74	-9	151	142	7	61	55	* H= 1 K= -3		
3	106	109	-7	72	90	9	143	147	-19	75	77
5	94	89	-6	94	86	11	92	83	-17	80	61
* H= 1 K=-12			-5	65	67	12	110	115	-16	124	138
-6	106	114	-4	92	83	15	76	64	-15	63	67
-4	74	70	-3	67	64	16	87	77	-14	151	153
-3	68	58	-1	59	54	* H= 1 K= -5			-11	172	167
0	73	70	1	100	101	-13	90	94	-10	120	119
* H= 1 K=-11			2	122	121	-12	78	87	-9	242	251
-10	77	72	4	59	40	-11	115	121	-7	192	197
-9	70	59	5	156	154	-10	102	95	-6	112	127
-8	74	69	7	185	197	-9	140	154	-4	152	119
-7	77	62	9	201	206	-7	277	287	-1	309	315
-6	98	92	11	134	145	-5	192	185	0	163	177
-4	159	156	12	77	64	-4	171	151	1	433	392
-2	195	192	13	89	75	-3	173	183	2	830	800
0	186	187	14	101	102	-2	241	233	4	142	177
1	172	174	16	115	100	-1	352	339	5	190	200
2	77	81	* H= 1 K= -7			0	360	358	6	304	286
3	129	123	-16	79	75	2	341	348	7	89	98
4	83	63	-14	62	61	3	64	66	8	305	313
5	87	79	-13	113	113	4	236	248	9	258	247
7	84	84	-12	106	101	5	60	84	10	224	232
9	82	83	-11	126	114	6	254	265	11	190	188
* H= 1 K=-10			-9	267	266	7	184	184	12	176	169
-6	125	122	-7	262	265	8	328	325	13	245	237
-5	65	43	-6	74	80	9	210	216	15	126	126
-3	67	60	-5	262	263	10	211	208	17	122	125
-2	123	143	-3	120	125	11	84	86	18	76	84
-1	107	92	-2	128	133	13	102	110	19	78	88

* H=	1	K= -2	-11	251	260	-7	95	106	-7	96	95
-18	90	80	-10	377	377	-5	160	159	-6	436	436
-16	87	106	-9	94	88	-4	172	154	-4	321	331
-15	101	112	-8	374	384	-3	233	226	-3	168	191
-14	89	101	-7	53	36	-2	99	89	-2	318	308
-13	73	65	-6	408	358	-1	57	58	-1	64	76
-12	375	376	-5	543	550	0	553	570	0	245	260
-10	365	374	-4	444	422	1	343	325	1	193	188
-8	269	280	-3	83	111	2	366	363	2	279	262
-7	405	386	-2	736	776	3	401	409	3	81	71
-6	370	375	-1	616	598	4	158	169	4	70	77
-5	492	447	0	74	50	5	215	227	6	74	83
-4	263	240	1	695	693	6	340	316	7	127	141
-3	135	143	2	355	375	7	310	296	8	51	28
-2	107	110	3	612	610	8	330	318	9	76	73
-1	411	409	4	267	276	10	401	412	12	156	150
0	351	358	5	167	157	12	321	324	13	93	91
1	119	75	6	235	245	15	104	99	14	99	113
3	243	215	8	243	237	16	99	102	17	81	61
4	100	109	10	303	311	17	106	107	19	79	65
5	152	171	12	74	61	18	79	72	* H=	1	K= 5
7	46	46	13	69	63	* H=	1	K= 3	-13	101	93
8	161	165	14	84	90	-17	136	131	-11	122	113
10	268	266	15	88	88	-15	143	162	-10	187	184
11	89	88	16	102	109	-13	171	183	-9	166	155
12	142	142	* H=	1	K= 1	-12	162	150	-8	255	279
13	231	230	-19	83	68	-11	124	128	-7	169	169
14	91	102	-15	71	57	-10	253	272	-6	376	381
15	210	204	-12	125	132	-9	169	186	-5	105	102
17	89	101	-11	54	36	-8	173	165	-4	389	409
19	104	93	-10	83	86	-7	148	147	-3	72	67
* H=	1	K= -1	-9	147	153	-6	197	191	-2	408	413
-15	74	62	-8	186	180	-3	172	151	-1	238	247
-14	165	162	-7	448	423	-2	156	135	0	166	179
-13	86	82	-6	230	214	-1	94	80	1	235	223
-12	273	274	-5	448	449	0	305	268	2	246	233
-10	244	241	-4	550	540	1	413	393	3	282	302
-9	216	216	-3	83	82	2	74	60	4	102	84
-8	375	391	-2	52	14	3	221	252	5	172	185
-7	211	203	-1	796	806	5	126	118	6	103	99
-6	678	659	1	787	780	6	171	168	9	63	73
-4	452	434	2	260	276	8	218	212	11	88	92
-3	293	310	3	384	361	9	219	206	12	62	74
-1	751	778	5	98	111	10	263	267	13	76	100
1	310	309	6	266	269	11	196	203	16	64	56
2	154	130	7	450	428	12	173	166	* H=	1	K= 6
3	344	332	8	316	330	13	103	93	-13	65	56
4	780	751	10	248	256	14	216	210	-11	104	112
6	121	94	11	88	83	15	91	91	-10	81	91
7	207	194	12	257	254	16	136	145	-9	75	60
8	334	333	14	193	201	19	95	83	-7	77	78
9	84	91	17	65	47	* H=	1	K= 4	-6	113	102
10	191	178	* H=	1	K= 2	-17	109	124	-5	79	99
12	131	143	-19	125	120	-15	109	109	-4	171	162
15	121	121	-17	116	118	-13	196	188	-3	64	77
19	101	94	-15	129	119	-12	77	63	-2	396	392
* H=	1	K= 0	-13	151	158	-11	234	232	-1	51	68
-16	96	103	-10	89	77	-10	136	143	0	244	246
-13	85	71	-9	186	197	-9	60	68	1	236	225
-12	62	62	-8	305	319	-8	294	290	2	386	379

3	251	256	-4	95	91	-1	73	80	-11	118	107
4	166	164	-2	130	134	0	106	99	-10	215	221
5	270	263	-1	64	69	1	264	268	-8	271	268
7	167	169	0	100	108	2	138	130	-6	255	259
8	162	174	1	91	88	3	131	137	-5	71	66
9	227	238	2	116	117	4	130	123	-4	326	336
11	80	67	* H= 1 K= 11			5	123	130	-3	346	335
13	63	46	-7	106	98	6	197	194	-2	257	246
14	65	65	-5	93	88	8	204	206	-1	289	302
* H= 1 K= 7			-3	132	116	9	61	45	1	345	356
-13	67	62	-2	110	108	10	154	147	2	113	110
-8	136	132	0	128	112	11	110	106	3	262	282
-6	71	79	2	129	136	12	96	89	4	63	53
-2	144	157	4	113	120	13	130	131	5	99	80
0	267	264	* H= 1 K= 12			15	98	94	7	149	142
2	215	223	0	97	79	* H= 2 K= -8			8	91	88
3	160	163	1	86	69	-15	101	82	11	67	78
5	230	226	2	95	95	-14	68	75	12	101	96
6	87	93	* H= 2 K=-13			-13	122	122	14	155	157
7	171	172	-1	82	53	-12	90	96	19	89	62
8	63	57	* H= 2 K=-12			-11	68	53	* H= 2 K= -5		
9	264	270	-7	107	98	-8	72	57	-14	77	81
10	69	58	-5	132	136	-6	95	91	-13	67	60
11	101	94	-3	99	101	-5	61	81	-11	106	103
12	80	91	-2	78	76	-3	72	79	-10	91	90
13	80	89	2	83	47	-2	135	119	-9	58	63
16	78	66	8	64	42	-1	142	148	-8	173	183
* H= 1 K= 8			* H= 2 K=-11			1	157	152	-6	376	373
-14	95	89	-9	103	85	3	64	55	-5	183	190
-11	107	96	-7	112	121	4	174	184	-4	360	373
-9	174	172	-5	101	97	6	169	171	-3	297	304
-7	105	106	-3	115	111	7	71	75	-2	292	299
-6	78	91	-1	227	221	8	90	87	-1	216	238
-5	73	84	0	90	95	10	240	255	0	314	326
-4	153	159	1	167	170	11	120	116	1	488	496
-3	89	85	2	144	154	12	217	214	2	52	49
3	65	57	4	101	101	15	132	131	3	446	429
4	113	106	6	96	93	17	94	96	4	112	116
6	118	127	8	71	72	* H= 2 K= -7			5	264	294
9	117	119	* H= 2 K=-10			-15	128	126	6	76	71
11	134	145	-11	75	61	-13	133	123	7	204	209
12	85	70	-9	89	75	-10	197	188	8	103	130
13	70	74	-7	96	104	-8	246	245	9	73	68
14	75	70	-5	128	136	-6	176	171	10	171	166
* H= 1 K= 9			-3	221	219	-5	171	168	11	103	104
-13	80	72	-1	194	191	-4	76	87	12	159	160
-12	78	77	1	168	164	-3	57	54	17	69	65
-11	153	152	2	210	219	-2	119	103	* H= 2 K= -4		
-9	126	127	3	109	96	1	179	190	-17	81	82
-7	80	76	4	205	205	2	111	122	-15	78	77
-6	69	73	5	105	93	3	261	260	-13	110	111
-5	120	117	6	103	94	4	123	117	-12	119	123
-3	97	93	8	111	121	8	94	73	* -10	125	129
0	168	172	10	118	109	10	156	151	-9	102	106
2	125	130	13	76	59	14	132	124	-8	59	62
13	79	44	* H= 2 K= -9			15	113	126	-7	50	43
* H= 1 K= 10			-12	70	61	17	94	101	-6	76	81
-9	122	107	-10	69	78	* H= 2 K= -6			-5	235	211
-7	166	164	-7	151	148	-13	78	95	-2	75	82
-5	122	131	-5	170	162	-12	137	143	-1	205	197

0	57	75	-8	162	164	-7	425	436	2	548	529
1	568	595	-7	329	325	-6	105	99	3	123	126
2	317	302	-6	288	269	-5	549	542	4	302	304
3	790	769	-5	101	73	-4	266	263	5	120	142
4	111	122	-4	450	421	-2	117	176	6	232	240
5	509	497	-3	201	217	-1	809	755	7	338	324
6	190	205	-2	678	659	0	1139	1097	8	198	207
7	422	415	0	56	67	1	170	158	9	163	174
8	248	259	1	270	290	2	370	356	11	245	257
9	204	215	2	257	247	3	382	381	12	106	106
10	277	282	3	294	291	4	322	305	13	206	197
11	77	84	4	397	371	5	270	282	14	129	135
12	153	155	5	263	250	7	179	199	15	161	164
14	143	141	6	119	99	8	63	38	16	65	71
16	92	100	7	96	84	9	87	83	20	85	65
18	67	66	8	60	52	11	275	278	* H= 2 K= 3		
* H= 2 K= -3			9	310	298	13	152	162	-18	109	100
-18	81	76	10	61	75	15	99	106	-16	143	135
-17	77	98	11	121	120	18	76	81	-14	156	158
-16	72	51	12	133	141	* H= 2 K= 1			-13	71	98
-15	134	142	13	84	87	-17	72	72	-12	164	159
-13	92	113	14	218	216	-15	124	128	-11	83	87
-11	151	151	16	126	133	-10	106	112	-9	213	215
-9	89	98	* H= 2 K= -1			-9	410	410	-7	293	293
-8	304	300	-17	103	110	-7	223	228	-5	131	132
-6	274	252	-16	85	84	-5	71	54	-3	62	62
-5	152	115	-15	115	128	-4	408	391	-2	112	111
-4	47	28	-13	138	144	-3	247	249	-1	119	109
-3	200	208	-11	367	373	-2	262	263	0	57	75
-2	206	190	-10	58	57	-1	154	135	1	189	173
-1	77	57	-9	282	282	0	403	399	2	299	286
0	510	518	-6	324	326	2	515	501	4	322	310
1	505	450	-5	197	190	3	482	489	5	175	194
2	114	139	-4	397	397	4	638	635	6	144	164
3	382	350	-3	326	311	5	143	144	8	104	89
4	95	81	-2	128	105	6	329	319	9	199	196
5	99	101	-1	156	166	7	479	461	11	274	293
6	123	115	0	339	335	8	237	204	12	57	52
7	138	152	1	166	183	9	207	219	13	155	150
8	130	128	2	914	907	10	172	165	16	105	99
9	330	333	3	592	570	11	270	265	17	77	75
10	247	241	4	213	189	14	68	68	18	12[illegible]	124
11	164	156	5	122	137	15	68	79	* H= 2 K= 4		
12	307	315	6	98	97	16	110	99	-16	83	75
13	99	102	9	94	93	* H= 2 K= 2			-16	115	116
14	206	193	10	143	146	-18	107	99	-14	124	129
15	80	94	11	174	180	-16	75	74	-12	186	191
16	105	114	13	75	58	-13	90	84	-11	107	131
17	101	94	14	192	187	-12	75	76	-10	173	186
18	111	107	15	85	80	-11	135	109	-9	209	204
19	99	90	18	92	94	-10	83	87	-8	134	144
* H= 2 K= -2			19	84	64	-9	136	131	-7	324	329
-17	97	97	20	82	71	-8	72	72	-5	257	265
-15	111	105	* H= 2 K= 0			-5	141	158	-4	65	77
-14	123	120	-17	71	68	-4	146	142	-3	131	133
-13	190	194	-15	101	113	-3	268	264	-2	213	226
-12	72	79	-13	116	116	-2	168	163	-1	96	92
-11	237	248	-12	124	113	-1	57	61	0	217	213
-10	201	196	-11	179	185	0	263	236	1	134	109
-9	194	186	-8	284	280	1	146	147	2	224	231

3	56	66	1	154	152	-10	76	67	9	208	202
4	198	205	2	182	189	-6	113	101	11	153	162
8	165	165	3	166	166	-4	151	149	12	115	113
9	127	132	4	187	185	-2	139	137	13	137	133
10	144	152	6	69	66	0	126	120	14	171	166
11	68	76	7	85	82	1	145	155	16	123	114
13	83	76	8	169	175	2	73	72	* H= 3 K= -7		
15	92	84	10	180	178	3	160	156	-14	115	119
* H= 2 K= 5			11	83	74	5	103	102	-13	104	107
-15	70	33	12	77	71	7	77	61	-12	136	136
-14	72	62	15	92	90	* H= 3 K=-10			-11	116	114
-12	90	96	* H= 2 K= 8			-8	94	101	-9	129	114
-10	159	158	-10	98	101	-6	182	171	-8	91	92
-9	126	121	-7	107	105	-4	122	115	-7	197	182
-8	151	162	-6	106	99	-2	144	141	-6	110	112
-7	300	315	-4	108	103	0	179	181	-5	152	150
-6	121	133	-1	79	79	1	118	110	-4	141	143
-5	351	348	0	77	68	2	137	150	-2	78	83
-3	396	402	1	111	124	3	236	239	-1	60	46
-2	130	150	5	117	116	5	226	238	0	144	154
-1	193	206	6	129	140	7	111	117	1	74	74
0	87	93	7	72	57	9	98	99	2	56	66
1	193	208	8	127	118	10	80	69	5	298	290
2	293	307	12	82	91	13	68	59	6	138	135
3	156	168	13	97	81	* H= 3 K= -9			7	84	76
4	137	133	* H= 2 K= 9			-11	67	56	8	114	103
5	175	174	-10	129	121	-10	87	74	10	83	74
6	171	183	-8	159	156	-9	82	69	11	172	169
8	151	154	-3	75	78	-8	91	85	12	84	92
13	138	148	-1	65	72	-7	66	59	13	176	166
* H= 2 K= 6			1	82	78	-6	78	74	16	81	81
-12	87	86	3	94	93	-4	125	126	18	102	111
-11	104	104	4	68	58	-2	172	173	* H= 3 K= -6		
-10	66	63	* H= 2 K= 10			0	122	105	-15	72	66
-9	178	195	-8	128	123	2	75	81	-12	83	85
-7	70	68	-6	99	106	3	177	187	-10	94	97
-6	136	121	-5	68	70	4	127	137	-9	311	305
-5	83	91	-4	145	142	5	215	213	-7	297	309
-4	72	63	-3	103	114	6	111	117	-6	83	80
-3	219	211	-1	88	95	7	176	173	-5	327	325
-1	290	297	1	106	107	9	227	238	-4	203	213
0	75	78	3	100	111	10	134	151	-3	271	264
1	217	215	* H= 2 K= 11			11	130	128	-2	311	310
2	150	152	-4	88	83	14	102	105	-1	222	233
3	135	136	-3	65	62	16	100	102	0	59	59
4	337	331	-1	98	94	* H= 3 K= -8			1	184	182
5	160	156	1	111	110	-11	119	125	2	281	302
6	282	280	3	110	114	-9	97	96	3	331	345
7	88	93	5	97	79	-6	127	129	4	287	300
8	67	71	* H= 3 K=-13			-4	133	139	6	72	82
9	137	152	-4	68	50	-3	68	71	9	67	72
10	141	142	* H= 3 K=-12			-2	57	48	10	72	82
14	82	69	-8	117	104	-1	69	65	11	101	105
* H= 2 K= 7			-6	89	99	0	76	69	13	69	70
-10	69	81	-4	94	94	1	72	76	15	81	80
-8	82	80	-3	75	57	2	284	284	16	70	80
-7	98	95	-1	66	50	3	61	49	17	76	64
-5	140	140	3	76	64	4	80	85	* H= 3 K= -5		
-3	92	80	* H= 3 K=-11			5	143	144	-13	87	97
-1	77	77	-11	73	59	7	155	150	-12	72	73

-11	144	147	-5	218	230	2	143	129	9	75	57
-10	59	58	-4	65	39	3	72	76	10	226	231
-9	127	149	-3	114	119	4	437	435	11	164	172
-8	62	51	-2	341	351	5	89	84	12	200	208
-7	182	176	-1	94	108	8	93	109	14	139	161
-6	49	36	0	86	79	9	56	55	* H= 3 K= 2		
-5	389	383	2	641	630	10	166	167	-17	87	79
-4	195	211	4	361	397	11	56	58	-16	73	51
-3	362	369	5	50	34	12	126	126	-15	89	86
-2	198	204	6	293	285	15	69	76	-14	92	100
-1	246	235	7	98	73	17	117	118	-13	78	61
0	258	285	8	278	276	19	104	116	-10	76	89
1	146	135	9	165	169	20	100	84	-9	129	122
2	460	494	10	80	78	* H= 3 K= 0			-8	272	279
3	299	309	11	251	254	-18	69	50	-5	92	92
4	216	224	13	279	287	-16	103	93	-4	132	143
5	72	79	15	162	154	-14	66	65	-3	111	139
6	185	202	17	127	142	-12	62	62	-2	147	145
7	355	348	18	74	73	-10	302	301	-1	57	76
8	72	71	19	92	64	-9	56	42	0	144	151
9	119	118	* H= 3 K= -2			-8	217	232	1	136	113
10	110	120	-17	71	74	-7	95	90	2	55	56
11	145	151	-16	117	113	-6	175	153	3	437	432
12	63	61	-14	121	124	-5	532	545	4	201	212
13	126	132	-12	255	251	-4	281	296	5	455	476
15	89	108	-10	249	245	-3	188	203	6	159	180
* H= 3 K= -4			-7	355	356	-2	89	87	7	127	96
-16	73	74	-5	255	233	-1	281	312	8	161	167
-12	73	76	-3	260	260	0	251	241	9	128	119
-9	162	163	-1	259	247	1	446	469	10	295	296
-8	138	132	2	110	100	2	256	235	12	240	240
-7	228	222	3	370	346	3	495	485	14	111	99
-6	151	159	4	348	334	4	346	351	15	137	143
-5	186	182	5	239	215	5	231	216	16	66	64
-3	251	242	6	126	134	6	403	405	17	98	106
-2	110	120	7	136	129	7	131	99	* H= 3 K= 3		
-1	151	148	8	133	144	10	174	182	-17	133	111
0	148	157	9	188	213	12	106	124	-15	156	154
1	353	366	10	247	249	14	84	88	-13	140	141
2	329	327	11	110	116	15	79	78	-12	112	103
3	92	80	12	73	80	16	113	102	-11	96	107
4	587	551	13	235	228	* H= 3 K= 1			-10	197	202
5	302	273	15	202	201	-16	66	71	-8	160	149
6	307	306	17	78	72	-14	87	87	-7	81	94
7	217	207	18	117	125	-11	112	117	-6	86	92
8	222	211	* H= 3 K= -1			-7	235	233	-5	71	58
9	266	263	-16	107	102	-6	209	216	-4	173	174
11	211	208	-14	143	137	-5	202	203	-3	127	133
13	203	205	-12	164	173	-4	305	303	1	150	159
14	101	86	-10	166	167	-3	330	295	2	87	85
15	99	101	-9	296	298	-2	201	205	3	314	335
17	95	92	-8	282	300	-1	450	453	4	274	270
19	93	85	-7	276	285	1	442	422	8	305	328
* H= 3 K= -3			-6	309	316	2	219	192	9	91	91
-16	102	107	-5	240	247	3	221	196	10	174	181
-14	94	110	-4	288	265	4	210	187	12	146	162
-10	111	111	-3	374	368	5	161	156	13	114	107
-9	126	123	-1	222	221	6	594	585	14	128	127
-8	88	86	0	188	161	7	329	316	15	65	56
-7	112	120	1	249	253	8	242	230	16	112	99

* H=	3 K=	4	4	137	143	-3	141	138	7	67	62
-15	114	101	5	261	265	-2	90	80	8	147	150
-13	102	109	6	67	66	-1	130	130	9	83	78
-11	141	146	7	75	98	0	85	80	10	173	177
-9	149	141	8	114	110	1	109	108	11	102	107
-8	206	215	9	122	137	2	113	122	12	178	180
-6	339	362	11	84	67	4	147	147	13	98	103
-4	211	230	13	77	68	6	86	85	14	70	36
-3	89	93	* H=	3 K=	7	7	67	69	15	137	127
-2	184	181	-7	96	89	* H=	4 K=-10		17	110	117
-1	221	210	-6	93	92	-10	74	53	* H=	4 K=	-7
0	51	40	-5	101	110	-7	86	90	-15	72	67
1	219	194	-2	129	135	-5	157	152	-13	99	107
2	78	97	-1	70	68	-3	197	197	-12	120	103
3	73	78	0	140	130	-1	143	147	-10	182	175
4	151	161	1	90	86	0	65	66	-8	142	143
5	86	81	2	86	80	1	119	128	-6	76	79
6	72	72	3	161	167	2	186	191	-5	187	196
7	176	180	5	222	236	3	60	54	-4	126	133
8	97	90	7	96	102	4	275	272	-3	152	157
9	61	64	8	67	64	5	66	55	-2	108	124
12	144	153	9	185	193	6	185	191	-1	67	71
14	115	112	10	84	76	8	149	148	0	165	176
17	96	85	11	89	100	10	75	80	2	116	124
* H=	3 K=	5	12	82	92	* H=	4 K=	-9	3	283	295
-15	79	86	13	96	81	-12	76	60	5	95	95
-13	105	112	* H=	3 K=	8	-10	79	73	6	115	123
-11	109	101	-11	71	69	-7	98	105	8	71	85
-10	101	98	-9	91	93	-5	77	86	10	99	94
-9	99	104	4	67	69	-4	73	75	12	63	58
-8	192	197	5	84	83	-3	132	131	13	87	85
-7	73	63	6	68	82	-1	129	133	14	107	115
-6	165	169	7	138	137	0	154	157	15	110	109
-4	239	228	9	103	111	1	198	199	* H=	4 K=	-6
-3	110	108	10	73	55	2	96	83	-15	83	52
-2	293	301	11	97	96	3	122	129	-14	100	99
-1	143	140	12	89	80	4	192	198	-12	83	80
0	96	84	* H=	3 K=	9	6	216	212	-11	100	96
1	114	123	-9	112	104	8	211	211	-10	61	54
2	73	63	-7	81	75	9	82	88	-9	80	87
3	301	304	-5	72	64	10	112	115	-8	225	226
4	90	79	-3	67	52	11	96	99	-7	63	75
5	209	225	0	87	86	12	124	123	-6	246	256
6	124	127	5	68	27	13	127	121	-5	135	140
7	104	115	* H=	3 K=	10	15	105	114	-4	186	210
9	90	93	-5	101	101	* H=	4 K=	-8	-3	267	268
* H=	3 K=	6	-4	85	85	-14	122	115	-2	74	81
-13	72	67	-2	118	114	-12	95	92	-1	320	332
-11	82	85	2	72	78	-10	68	84	1	317	328
-10	79	71	* H=	3 K=	-13	-9	86	77	3	113	91
-9	70	72	-4	73	81	-8	112	109	4	174	176
-8	106	97	4	88	83	-7	84	84	6	144	150
-6	170	173	* H=	4 K=	-12	-5	87	83	7	203	206
-4	165	150	-7	99	90	-3	83	96	9	138	139
-2	190	194	-5	98	103	0	56	61	10	67	73
-1	96	93	-3	95	81	1	66	70	11	69	64
0	162	174	* H=	4 K=	-11	3	57	72	12	131	124
1	238	252	-9	87	87	4	202	206	14	102	114
2	184	186	-7	114	113	5	103	101	19	73	73
3	199	192	-5	123	116	6	163	175	* H=	4 K=	-5

-14	72	72	-6	221	230	1	65	69	15	116	116
-13	70	66	-5	87	75	2	230	213	16	82	81
-12	72	89	-4	150	141	3	129	130	* H=	4 K=	2
-11	108	114	-3	107	107	4	255	217	-16	92	83
-10	196	204	-2	81	96	5	191	187	-13	106	110
-8	213	221	3	248	254	6	85	90	-11	85	96
-6	140	137	5	357	346	8	64	68	-7	71	84
-5	88	94	6	66	77	9	64	43	-6	179	184
-4	241	233	7	363	371	10	56	64	-5	81	66
-3	246	253	8	290	296	11	62	67	-4	137	130
-2	262	280	9	185	193	14	182	179	-3	69	64
-1	258	266	10	197	193	16	70	81	-2	70	73
0	121	131	11	154	160	19	84	63	0	119	126
1	152	151	12	366	379	20	93	77	2	250	257
2	202	184	14	290	286	* H=	4 K=	0	3	82	86
3	316	314	16	71	65	-15	100	99	4	220	210
4	49	40	17	94	103	-13	125	121	5	258	257
5	528	554	18	76	74	-9	97	105	6	169	174
6	204	189	* H=	4 K=	-2	-8	154	166	7	375	377
7	108	95	-17	78	69	-7	314	318	8	203	206
8	121	121	-15	138	133	-6	263	256	9	153	162
10	107	104	-13	148	148	-5	270	289	11	201	197
11	97	117	-11	122	123	-4	369	377	12	110	116
12	106	109	-10	124	113	-3	162	154	13	134	143
15	72	58	-9	203	205	-2	301	282	14	111	120
16	82	71	-8	168	170	-1	201	221	15	106	116
17	69	69	-7	120	128	0	291	306	16	86	75
* H=	4 K=	-4	-6	162	156	1	218	205	* H=	4 K=	3
-15	70	74	-5	115	119	2	336	306	-14	91	91
-14	71	71	-4	134	156	3	227	217	-12	90	96
-12	79	84	-3	52	67	4	267	264	-11	86	74
-10	64	56	-2	257	270	5	339	350	-9	154	163
-9	93	93	-1	106	117	6	182	173	-7	185	196
-8	92	87	0	141	139	7	116	102	-5	103	115
-6	198	202	3	88	89	8	161	162	-3	86	88
-4	252	264	5	104	122	9	55	64	-2	53	64
-2	224	208	6	112	103	10	90	100	-1	104	97
-1	156	148	7	129	147	11	130	131	0	91	100
0	120	116	9	183	161	13	79	86	2	71	77
1	406	397	10	168	167	* H=	4 K=	1	3	161	161
2	100	81	11	80	74	-17	68	56	4	217	230
3	585	607	12	161	163	-15	99	103	6	301	310
4	61	55	14	196	201	-9	154	160	7	58	55
5	268	270	15	59	11	-6	64	57	8	77	65
6	334	333	16	218	216	-4	242	246	9	101	102
7	227	232	18	126	126	-3	155	161	11	176	180
8	236	246	* H=	4 K=	-1	-2	278	284	13	126	130
9	75	87	-17	73	70	-1	71	66	14	79	84
10	227	227	-16	69	64	0	540	532	16	92	93
12	134	143	-13	143	140	1	230	223	17	81	81
13	62	47	-11	234	240	2	261	272	18	101	102
14	153	153	-9	247	240	3	302	319	* H=	4 K=	4
15	77	68	-8	134	136	4	390	415	-14	114	121
16	81	84	-6	410	429	5	237	237	-13	97	82
18	92	87	-5	125	131	6	100	103	-12	74	80
* H=	4 K=	-3	-4	371	376	7	301	308	-11	81	75
-15	102	93	-3	112	132	9	200	203	-10	76	77
-11	91	91	-2	430	421	11	190	186	-9	70	62
-8	182	194	-1	102	100	13	92	100	-8	136	125
-7	58	39	0	231	234	14	65	63	-7	186	192

-5	212	230	4	98	86	5	216	231	-13	80	89
-4	155	141	6	119	122	6	63	72	-11	100	98
-3	205	212	8	110	97	7	193	203	-10	64	43
-2	64	52	* H= 4 K= 9			9	182	186	-9	209	222
-1	69	67	-10	98	87	10	85	93	-7	203	199
2	185	196	-8	89	106	11	129	125	-6	112	101
4	115	131	5	65	58	12	74	73	-5	96	103
5	87	81	* H= 4 K= 10			14	92	95	-4	302	311
8	100	134	-6	109	91	16	114	105	-3	161	158
10	117	110	-4	111	93	* H= 5 K= -8			-2	292	288
11	81	107	-3	79	78	-13	77	79	-1	78	89
13	105	105	* H= 4 K= 11			-11	128	132	1	137	145
15	87	84	1	85	82	-9	89	99	2	169	163
* H= 4 K= 5			* H= 5 K=-14			-8	78	65	3	198	203
-12	102	101	-1	74	32	-6	119	111	4	209	220
-11	73	55	3	98	100	-4	130	135	5	62	55
-10	121	118	5	77	57	-3	61	62	8	93	96
-9	137	138	8	112	94	-1	78	79	9	69	78
-7	239	233	* H= 5 K=-13			2	210	205	10	110	110
-5	226	212	8	76	56	4	71	72	11	71	74
-3	213	203	12	96	85	5	109	105	13	100	106
-2	141	146	* H= 5 K=-12			7	272	277	14	97	88
-1	106	100	-4	83	73	8	59	62	16	86	97
0	155	160	-2	79	73	9	136	132	17	71	52
1	128	129	-1	77	64	10	75	90	* H= 5 K= -5		
2	140	135	14	71	54	11	128	130	-13	105	81
4	68	71	* H= 5 K=-11			12	148	137	-11	118	112
6	184	187	-9	77	83	13	106	105	-9	88	100
8	143	143	-8	76	79	14	152	147	-7	134	139
13	81	68	-6	136	128	16	113	96	-6	156	158
* H= 4 K= 6			-4	123	141	18	80	78	-5	278	279
-8	71	57	-3	74	76	* H= 5 K= -7			-4	178	175
-7	90	94	-2	117	119	-15	78	81	-3	251	245
-6	92	98	-1	85	85	-14	72	48	-2	251	256
-5	122	126	0	37	73	-13	109	107	-1	195	197
-3	207	198	1	68	80	-11	78	78	0	430	431
-2	86	87	3	86	93	-9	66	76	2	275	281
-1	231	247	5	131	129	-8	60	49	3	144	146
0	117	123	* H= 5 K=-10			-7	219	214	4	192	202
1	136	139	-13	75	39	-6	81	73	5	166	163
2	188	195	-8	76	56	-5	105	111	6	213	223
3	84	76	-6	107	108	-4	90	94	7	347	357
4	282	294	-4	155	140	-3	56	46	8	83	75
6	143	146	-2	186	194	-2	141	141	9	118	116
9	70	62	-1	82	86	0	122	143	14	95	92
* H= 4 K= 7			0	180	184	1	106	101	15	99	76
-5	111	111	1	139	146	2	80	70	* H= 5 K= -4		
-3	94	106	3	170	171	5	266	272	-9	79	80
-1	84	92	5	244	245	6	101	115	-7	177	183
0	92	110	7	144	160	7	133	132	-5	124	128
1	66	61	9	104	106	8	61	70	-3	205	211
2	97	102	* H= 5 K= -9			9	64	64	-2	144	142
3	97	102	-5	77	66	10	62	60	-1	236	239
4	171	177	-4	103	93	11	96	92	0	216	232
5	65	77	-2	145	155	12	95	99	1	76	71
6	126	127	0	113	114	13	74	90	2	321	328
8	133	143	1	104	122	14	90	85	4	428	443
10	111	100	2	91	71	16	135	130	5	217	207
* H= 4 K= 8			3	203	222	18	122	111	6	332	350
-12	78	68	4	114	96	* H= 5 K= -6			7	139	130

8	183	190	3	61	65	17	111	110	14	145	156
9	194	197	4	206	209	* H= 6 K= -5			16	71	73
11	173	175	6	185	176	-12	103	88	17	94	73
13	139	152	8	199	205	-10	136	131	18	86	88
* H= 5 K= -3			10	143	138	-8	179	178	* H= 6 K= -2		
-16	96	85	11	92	99	-6	104	104	-15	76	85
-14	99	106	12	96	87	-5	164	153	-13	84	89
-13	67	71	* H= 6 K= -6			-4	60	78	-11	105	114
-8	102	104	-12	81	57	-3	245	257	-9	130	139
-5	115	117	-10	79	73	-2	181	177	-8	85	85
-4	98	81	-9	66	77	-1	246	255	-7	62	57
-2	217	236	-3	95	91	0	160	147	-6	69	63
-1	122	129	-1	89	90	1	293	298	-5	97	104
0	88	107	1	97	97	2	79	89	-3	154	148
2	187	196	4	111	106	3	366	371	-2	86	92
4	220	219	5	173	184	5	290	304	-1	127	131
6	359	361,	6	240	259	6	64	60	0	155	170
7	131	141	8	262	263	7	94	91	1	112	122
8	263	251	9	151	157	8	121	119	3	73	72
9	199	205	10	116	118	10	137	129	5	150	145
10	208	199	11	151	141	* H= 6 K= -4			6	123	115
11	143	155	12	93	95	-12	80	72	7	115	124
13	239	250	13	128	113	-10	66	63	8	174	160
15	196	187	15	117	112	-7	63	63	9	184	194
17	99	115	17	91	93	-6	137	134	10	200	202
* H= 6 K=-13			* H= 6 K= -7			-5	122	109	11	93	90
4	66	45	-12	122	119	-4	273	284	12	93	95
* H= 6 K=-12			-10	100	108	-3	126	138	14	132	134
-5	101	80	-8	105	99	-2	182	181	16	158	156
0	70	70	-6	65	66	-1	256	257	18	91	87
7	77	64	-5	202	210	0	58	71	* H= 6 K= -1		
* H= 6 K=-11			-4	68	43	1	199	208	-13	117	121
-9	83	60	-3	98	92	3	255	269	-11	138	150
-7	113	115	-2	78	86	4	58	27	-10	70	64
-5	126	120	3	72	69	5	184	190	-9	136	120
-3	132	122	5	94	85	6	221	222	-7	69	73
-2	82	82	8	59	59	7	260	271	-6	226	229
-1	81	86	9	95	103	8	272	276	-4	177	187
1	73	80	10	171	157	9	106	121	-2	137	150
4	96	94	11	97	106	10	63	60	0	111	113
6	73	67	12	116	116	14	187	173	1	79	71
* H= 6 K=-10			13	158	163	* H= 6 K= -3			2	76	66
-5	133	110	14	105	87	-13	85	90	4	57	52
-3	184	190	15	157	152	-12	95	85	5	159	174
-1	193	187	17	107	110	-8	67	62	7	111	118
0	119	124	* H= 6 K= -6			-6	95	104	8	64	65
1	110	106	-12	116	116	-3	112	101	9	153	156
2	115	113	-10	95	100	-2	105	105	12	71	81
4	139	145	-9	187	182	-1	84	80	14	121	121
6	149	152	-7	71	63	0	116	116	16	107	91
7	71	51	-6	255	246	1	169	173	* H= 6 K= 0		
8	96	90	-5	75	68	3	219	222	-15	85	88
* H= 6 K= -9			-4	136	121	4	103	101	-13	123	110
-7	108	109	-3	188	199	5	241	249	-11	108	119
-5	95	116	-1	268	273	6	103	107	-9	133	130
-3	112	106	1	136	134	7	281	283	-6	74	74
-1	126	135	4	110	99	8	101	104	-7	133	156
0	158	157	6	107	116	9	95	101	-6	136	137
1	175	176	7	124	119	10	169	172	-5	136	126
2	135	150	15	74	75	12	218	220	-4	185	206

-2	278	292	-11	94	96	* H=	7 K=	-9	9	160	170					
-1	63	71	-10	92	76	-6	70	64	11	93	99					
0	186	214	-9	90	93	-4	100	105	12	66	52					
1	111	100	-8	66	57	-2	123	117	14	73	72					
2	153	151	-7	88	82	0	116	108	16	74	66					
3	153	140	-5	100	101	1	85	84	18	76	66					
5	173	180	-3	133	133	2	137	132	* H=	7 K=	-5					
6	104	110	0	60	50	3	165	171	-13	81	56					
8	84	77	7	83	94	4	105	94	-9	103	104					
10	71	76	8	104	109	5	200	202	-7	176	165					
18	83	87	9	113	65	7	137	181	-6	97	106					
* H=	6 K=	1	11	68	61	8	82	74	-5	221	219					
-11	100	92	15	87	82	9	125	128	-4	129	131					
-9	87	92	* H=	6 K=	5	10	108	122	-3	98	87					
-7	120	118	-10	98	69	12	66	64	-2	161	170					
-6	88	80	-9	89	84	* H=	7 K=	-8	-1	73	93					
-4	315	318	-7	153	149	-8	70	61	0	230	231					
-2	213	224	-5	125	121	-4	67	74	1	70	63					
0	230	233	-2	66	61	-1	76	77	2	212	223					
1	106	102	0	74	63	0	111	109	4	78	82					
2	259	279	1	88	89	1	105	114	5	118	111					
3	179	174	2	62	71	2	93	98	7	118	125					
4	189	196	8	102	103	3	75	65	8	81	77					
5	173	169	* H=	6 K=	6	4	71	70	11	84	90					
7	159	165	-7	77	83	5	93	96	12	62	51					
9	70	77	-5	104	98	6	82	83	13	64	53					
10	77	75	-3	142	142	7	289	289	* H=	7 K=	-4					
11	83	94	-2	83	71	9	226	214	-7	81	66					
* H=	6 K=	2	-1	134	125	10	119	111	-5	95	110					
-13	74	59	2	100	106	11	112	106	-4	125	130					
-11	77	55	4	139	132	12	76	78	-3	144	142					
-6	68	66	6	103	78	13	72	70	-2	243	254					
-2	104	93	8	69	60	14	90	79	-1	162	166					
-1	67	55	9	65	40	* H=	7 K=	-7	0	236	239					
0	218	211	* H=	6 K=	7	-11	83	77	2	257	246					
2	188	197	-3	75	87	-9	73	71	4	259	245					
4	182	193	-1	73	75	-7	142	150	5	63	74					
5	203	196	1	78	76	-4	70	65	6	261	251					
6	259	260	2	72	82	-2	121	120	7	119	122					
7	326	325	4	136	131	0	74	86	9	122	126					
8	119	143	6	107	110	3	75	86	10	63	68					
9	196	202	8	93	83	5	154	157	11	113	112					
10	64	67	* H=	7 K=	-12	9	128	130	13	84	81					
11	105	93	10	95	86	11	104	114	* H=	7 K=	-3					
* H=	6 K=	3	* H=	7 K=	-11	12	76	61	-11	80	73					
-13	81	53	-6	89	88	13	106	107	-9	73	62					
-4	79	79	-4	116	103	14	84	91	-5	82	92					
-2	111	110	-3	79	70	16	121	117	-4	58	58					
0	102	101	-1	81	81	* H=	7 K=	-6	-3	140	133					
4	120	125	* H=	7 K=	-10	-11	113	120	-2	110	101					
5	68	73	-8	117	96	-9	134	137	-1	111	98					
6	144	147	-5	70	53	-7	130	126	0	104	110					
7	112	110	-4	141	140	-5	88	89	2	178	169					
9	78	76	-2	154	143	-4	166	165	4	200	187					
10	75	73	-1	86	86	-3	125	118	5	131	130					
11	164	152	0	152	150	-2	132	129	6	131	130					
13	113	115	1	130	136	-1	82	72	7	261	251					
15	73	61	3	122	110	0	66	53	8	142	131					
16	77	64	5	119	119	3	61	64	9	215	211					
* H=	6 K=	4	7	78	71	7	63	75	10	154	154					

11	96	87	-6	125	139	-1	77	74	8	144	159
13	133	153	-5	112	114	0	93	84	10	70	79
15	115	114	-3	156	150	1	96	102	13	71	66
* H= 7 K= -2			-2	61	47	3	109	96	15	104	110
-14	71	53	-1	214	207	7	76	66	* H= 8 K= -6		
-12	78	78	1	209	211	* H= 7 K= 7			-10	74	89
-10	82	81	3	124	121	3	83	83	-8	129	120
-9	76	78	4	103	98	* H= 8 K=-11			-6	137	142
-7	72	84	5	73	60	-3	103	96	-2	75	79
-5	67	71	6	213	215	-2	77	93	-1	99	105
-2	99	104	8	78	98	0	116	111	1	71	76
-1	64	62	10	121	119	2	73	76	3	61	64
0	54	41	11	81	87	* H= 8 K=-10			4	66	68
1	86	73	13	70	60	-5	104	118	7	91	75
6	205	201	* H= 7 K= 2			-3	106	114	10	68	64
8	163	173	-11	72	20	-1	100	107	12	86	83
9	161	168	-5	85	76	0	86	88	17	82	78
11	148	167	-3	152	150	1	108	113	* H= 8 K= -5		
13	176	187	-2	115	98	2	124	125	-10	91	102
15	95	100	-1	133	140	4	122	133	-3	129	144
17	78	81	1	113	127	5	67	55	-6	80	93
* H= 7 K= -1			3	129	139	6	73	67	-4	70	73
-12	102	97	4	84	89	7	84	84	-3	133	136
-10	96	106	5	108	101	* H= 8 K= -9			-2	97	92
-9	77	79	6	94	104	-9	69	51	-1	132	141
-7	113	109	8	127	128	-3	76	68	1	139	144
-5	125	114	10	165	150	-1	73	69	2	109	120
-4	65	64	11	93	79	0	101	95	3	130	119
-3	145	149	12	89	70	2	92	81	4	74	76
-1	131	134	15	88	66	3	75	71	8	92	88
4	84	89	* H= 7 K= 3			4	134	140	10	158	160
5	75	72	-4	81	80	6	156	148	* H= 8 K= -4		
7	78	75	-3	71	68	8	151	151	-6	112	109
8	62	65	-1	91	99	9	79	91	-4	169	165
9	131	130	1	123	125	10	82	80	-3	76	83
10	100	110	3	124	108	11	110	111	-2	86	80
11	69	67	5	122	113	* H= 8 K= -8			-1	159	158
12	61	53	6	91	109	-3	91	94	1	225	217
15	90	109	8	74	89	-1	84	82	3	209	212
* H= 7 K= 0			12	81	98	0	60	54	5	124	120
-10	114	108	13	77	55	1	126	125	6	221	215
-8	101	106	14	91	70	2	99	106	7	70	75
-7	102	89	* H= 7 K= 4			3	81	95	8	131	133
-6	76	72	-8	83	78	4	112	106	9	113	107
-5	180	185	-6	66	44	6	114	125	12	64	42
-4	133	127	-3	81	75	8	121	127	14	69	69
-3	255	247	-1	108	96	9	88	79	17	75	30
-1	183	183	7	83	82	10	80	73	* H= 8 K= -3		
0	123	123	10	74	65	11	79	70	-6	61	54
1	190	204	12	72	71	12	74	65	-2	93	101
2	165	167	* H= 7 K= 5			13	92	98	-1	159	164
3	63	61	-6	74	79	15	93	76	0	117	110
4	95	95	-4	90	90	* H= 8 K= -7			1	139	146
5	108	103	-3	75	72	-10	85	77	3	174	182
8	105	113	-2	70	69	-3	81	84	4	88	74
12	73	50	-1	80	62	-1	109	107	5	220	205
17	72	56	3	68	64	0	89	93	6	97	93
* H= 7 K= 1			* H= 7 K= 6			1	79	80	7	134	143
-10	84	72	-4	73	78	3	62	67	8	94	85
-8	85	86	-2	78	82	6	87	95	9	82	74

10	156	163	-6	75	73	-2	75	79	* H= 9 K= -4		
12	121	110	-4	129	125	1	99	79	-4	70	52
14	71	65	-2	101	102	3	128	127	-3	87	78
* H= 8 K= -2			0	131	123	5	120	116	-2	129	120
-10	76	72	1	111	117	7	90	91	-1	136	128
-8	89	79	2	109	105	9	94	90	0	160	159
-3	113	111	3	78	67	10	105	97	2	186	178
5	104	114	4	64	62	12	81	62	3	81	72
7	100	101	5	74	74	* H= 9 K= -8			4	158	149
8	184	168	7	103	107	1	84	85	5	67	71
9	100	109	9	143	135	2	75	68	6	94	97
10	98	103	11	82	76	3	114	110	7	100	107
11	144	142	15	77	33	5	126	109	9	135	136
12	150	144	* H= 8 K= 2			7	138	134	* H= 9 K= -3		
14	110	120	-7	72	59	9	92	103	-7	71	66
15	71	59	-2	72	74	10	84	69	-5	65	59
16	78	63	0	121	121	11	103	89	-3	77	61
* H= 8 K= -1			2	123	118	12	122	113	0	92	105
-11	86	86	3	106	101	14	85	80	2	155	155
-10	72	52	4	93	81	* H= 9 K= -7			4	137	133
-9	70	78	5	167	160	-2	81	90	6	71	68
-8	68	76	7	127	119	0	77	76	7	106	87
-6	91	95	9	116	110	2	60	51	8	100	97
-2	64	78	11	74	74	7	85	89	9	121	119
-1	88	87	* H= 8 K= 3			10	69	50	10	89	63
0	91	97	7	102	95	11	75	76	11	71	77
1	131	142	9	113	100	12	73	51	13	117	98
7	100	94	11	118	110	13	83	71	* H= 9 K= -2		
12	68	55	* H= 8 K= 4			14	77	84	-2	107	104
16	89	87	4	66	40	* H= 9 K= -6			0	83	77
* H= 8 K= 0			7	80	78	-9	77	77	1	77	61
-9	83	86	* H= 9 K=-11			-7	72	74	6	104	115
-7	72	84	-1	77	69	-6	91	74	11	128	118
-6	72	71	1	107	92	-4	112	110	13	115	120
-5	74	59	* H= 9 K=-10			-2	96	90	* H= 9 K= -1		
-4	122	123	-4	109	92	0	77	66	-9	71	50
-2	191	181	-3	86	54	2	70	54	-7	69	58
0	115	123	-2	98	82	9	69	64	-1	82	85
2	108	100	-1	91	84	* H= 9 K= -5			2	82	69
3	106	101	0	74	83	-9	75	76	4	90	93
5	90	100	1	84	85	-7	111	109	11	75	62
14	66	45	2	65	42	-5	108	101	15	79	67
* H= 8 K= 1			5	83	86	-2	127	124			
-9	91	87	* H= 9 K= -9			0	164	150			
-7	74	74	-4	84	76	2	124	125			

TABLE 4.21 STRUCTURE FACTORS for $(RhL_3CO(H_2O))^+ PF_6^-$

* H= 0 K= 0			-8	536	574	9	834	880	-5	700	707
1	140	172	-7	739	788	* H= 0 K= 7			-4	843	851
2	3394	3499	-6	590	632	-8	551	540	-3	844	855
3	1733	1669	-5	1446	1410	-6	635	669	-2	1453	1476
4	606	564	-4	856	839	-3	857	833	0	1461	1483
5	725	696	-3	229	186	-1	961	930	1	665	622
6	495	452	-2	683	754	0	592	648	2	1124	1241
7	1486	1549	-1	984	767	1	800	829	3	1074	1022
8	498	515	0	420	347	2	787	746	4	448	458
9	1192	1145	1	422	287	4	1261	1282	5	1479	1547
10	357	368	2	2016	1990	6	1195	1270	7	398	961
12	644	815	3	2161	1908	9	580	549	10	513	491
13	294	175	4	424	453	* H= 0 K= 8			* H= 1 K= -6		
14	446	390	6	961	712	-10	774	559	-7	880	951
* H= 0 K= 1			* H= 0 K= 4			-6	451	539	-6	853	915
-11	421	463	-14	565	325	-4	623	634	-5	1192	1216
-10	590	588	-11	722	763	-3	892	926	-4	1082	1090
-9	848	829	-10	603	598	4	729	775	-2	388	801
-8	317	301	-8	793	901	6	448	519	0	2201	2220
-7	1261	1317	-7	1174	1213	* H= 0 K= 9			1	655	712
-6	240	184	-6	1080	1029	-8	684	611	2	699	743
-5	1521	1473	-4	1421	1475	-3	771	539	3	1857	1831
-4	1250	1141	-3	475	489	-2	413	523	5	1286	1226
-3	2095	1998	-2	737	814	-1	474	537	7	1084	1125
-2	3106	3271	-1	866	852	* H= 0 K= 10			8	1129	1110
-1	1031	1259	0	413	437	-7	756	745	10	806	829
0	2273	2127	1	926	878	-6	576	220	* H= 1 K= -5		
1	603	645	2	283	324	-2	781	761	-7	869	841
2	947	980	3	493	440	-1	652	742	-6	1011	995
3	1868	1914	4	1020	1166	0	745	665	-5	551	537
5	1587	1547	5	776	860	* H= 0 K= 11			-4	399	435
7	1280	1349	6	1391	1359	-4	595	566	-1	443	286
8	762	762	* H= 0 K= 5			-2	761	742	0	485	557
9	775	804	-9	787	811	0	777	812	1	1178	1132
10	1636	1699	-8	1365	1475	* H= 0 K= 12			3	1495	1511
11	469	489	-6	1914	1931	-5	636	398	4	1165	1211
12	933	933	-5	961	820	* H= 1 K=-12			5	1081	1189
14	594	640	-4	1438	1410	3	442	455	6	1803	1806
* H= 0 K= 2			-3	822	726	* H= 1 K=-11			7	1051	995
-14	335	345	-2	569	357	1	469	484	8	809	790
-12	576	558	-1	1870	1733	* H= 1 K=-10			9	726	748
-11	323	249	1	1979	1474	1	571	559	10	650	666
-10	495	437	2	1491	1454	2	690	761	* H= 1 K= -4		
-7	999	964	3	1659	1657	4	734	636	-5	429	536
-6	445	438	4	1490	1535	* H= 1 K= -9			-4	457	513
-5	798	862	5	1102	1090	-3	622	449	-3	724	775
-3	696	637	6	783	755	3	519	553	-1	1041	1155
-2	336	395	* H= 0 K= 6			5	537	614	1	1266	1141
1	2733	2699	-13	599	445	7	609	647	3	884	874
2	2126	2231	-8	1069	1044	* H= 1 K= -8			4	993	992
3	2754	2797	-6	1369	1544	-7	710	693	6	1214	1138
4	504	563	-4	962	1042	-5	703	649	10	574	514
5	1136	1123	-3	1522	1568	-3	629	679	11	809	810
6	960	933	-1	1174	1180	-2	1126	1116	* H= 1 K= -3		
8	1117	1141	1	1365	1503	0	999	991	-11	710	701
10	1057	1123	2	1721	1699	5	1015	1000	-10	464	437
-2	631	637	3	972	911	7	732	755	-9	721	697
* H= 0 K= 3			4	1106	1081	* H= 1 K= -7			-8	576	576
-11	507	492	6	1267	1275	-9	640	625	-7	391	411
-9	635	567	8	1131	1129	-7	1235	1267	-6	1052	987

-5	390	397	1	425	253	2	450	598	-8	721	536
-4	2010	2033	2	4162	4430	3	906	879	-6	828	660
-3	1187	1037	3	1814	1865	4	848	846	-1	583	443
-2	1522	1377	4	766	819	6	544	525	* H= 1 K= 9		
-1	2523	2439	5	804	812	8	996	1005	-8	810	849
0	3084	2788	6	1499	1453	10	628	671	-7	622	441
1	340	439	7	1364	1425	* H= 1 K= 4			-5	731	771
3	1742	1661	9	1494	1496	-11	771	749	-3	954	966
4	377	373	11	1303	1311	-9	1238	1253	-1	889	904
5	319	419	12	475	507	-7	2343	2338	1	638	654
6	640	595	13	644	385	-6	771	830	* H= 1 K= 10		
7	560	560	* H= 1 K= 1			-5	1340	1408	-5	780	759
8	476	453	-11	554	580	-4	656	724	-3	744	771
9	751	717	-8	485	453	-2	2224	2197	2	325	868
* H= 1 K= -2			-7	506	562	0	1863	1758	* H= 1 K= 11		
-13	754	720	-5	598	549	1	1726	1764	-2	892	575
-11	675	611	-4	1181	1275	2	757	796	5	501	517
-10	752	760	-3	381	406	3	1552	1404	* H= 2 K=-12		
-8	1895	1976	-2	1290	1377	5	1423	1392	-1	671	330
-6	1570	1604	-1	646	597	6	1274	1279	* H= 2 K=-11		
-5	1071	1071	0	1023	975	7	1001	994	4	841	576
-4	1347	1408	1	1553	1490	8	647	608	* H= 2 K= -9		
-3	2570	2524	2	2381	2489	* H= 1 K= 5			-8	617	614
-2	287	325	3	1700	1684	-9	1030	998	-3	729	779
-1	4489	4493	4	1355	1186	-7	1399	1446	-1	841	862
1	2843	2811	5	1040	1041	-5	557	541	2	771	739
2	1977	1895	7	1312	1341	-4	1002	1175	4	637	600
3	614	475	9	1036	1042	-3	1060	1013	7	685	587
4	1135	1104	12	723	719	-2	1175	1162	* H= 2 K= -8		
6	1297	1450	14	815	632	-1	1519	1586	-8	768	798
7	1282	1299	* H= 1 K= 2			0	963	905	-6	500	476
8	746	776	-10	747	757	1	1166	1194	-5	869	887
9	1090	1111	-9	821	809	2	905	933	-4	785	600
* H= 1 K= -1			-8	969	968	3	2468	2486	-3	875	899
-10	1187	1142	-7	510	528	4	1455	1520	-1	1207	1268
-8	942	919	-3	1537	1350	5	2064	2162	0	1092	1109
-7	588	480	-2	578	804	6	646	828	1	826	630
-6	1611	1514	-1	2971	3077	7	1145	1145	2	1359	1350
-5	1430	1431	0	1709	1706	8	476	516	3	652	682
-4	835	936	1	264	197	10	743	733	4	1069	1016
-3	4582	4427	2	1925	1725	* H= 1 K= 6			7	797	793
-2	316	153	3	2300	2241	-6	636	783	9	385	895
-1	4419	4405	4	222	45	-4	1599	1405	* H= 2 K= -7		
0	588	600	5	1395	1361	-2	569	465	-3	601	632
1	2071	1999	6	683	687	-1	854	884	-7	550	587
2	2932	3101	12	705	665	0	625	617	-6	630	668
4	2679	2599	* H= 1 K= 3			1	1034	1020	-2	925	961
6	1[illegible]	[illegible]	-12	572	718	3	2[illegible]	2[illegible]	-1	550	560
7	920	907	-11	902	717	4	630	587	0	1453	1474
8	658	721	-10	1[illegible]	1[illegible]	5	1[illegible]	1[illegible]	1	1[illegible]	1[illegible]
9	1221	1[illegible]	-9	950	954	6	8[illegible]	8[illegible]	3	899	861
11	1140	1179	-7	552	677	8	681	674	4	1[illegible]	1[illegible]
13	750	762	-6	745	715	10	610	605	5	599	644
* H= 1 K= 0			-5	798	865	* H= 1 K= 7			6	1201	1231
-8	487	479	-4	1441	1534	-9	606	577	7	827	827
-6	1444	1471	-3	1153	1209	-4	530	579	8	776	630
-5	1430	1470	-2	1057	1165	-2	746	782	9	581	611
-3	3190	3274	-1	1105	1172	3	485	464	* H= 2 K= -6		
-1	1071	1103	0	2701	2699	6	713	665	-5	564	556
0	1974	1915	1	1364	1355	* H= 1 K= 8			-4	1013	966

-3	542	553	-12	592	334	-11	885	886	-3	1607	1666
-2	566	574	-11	856	812	-7	633	610	-2	1184	1179
0	1085	1113	-9	439	465	-4	1653	1622	-1	343	329
2	1157	1130	-8	424	464	-3	1333	1270	0	2156	2160
3	843	885	-7	873	922	-2	913	868	2	2792	2903
4	656	717	-6	2066	1962	0	2474	2287	3	1748	1750
5	1389	1472	-4	2222	2265	1	365	228	4	2445	2439
6	904	926	-3	1181	1136	2	360	441	5	452	478
7	796	797	-2	2547	2444	4	790	701	6	383	456
10	790	747	-1	1015	909	5	732	675	7	443	429
12	689	672	0	1699	1611	6	648	657	9	943	986
* H= 2 K= -5			1	3450	3465	7	652	623	10	715	762
-5	451	461	2	2428	2246	9	1076	1068	12	681	666
-4	439	362	3	2097	2190	* H= 2 K= 2			* H= 2 K= 5		
-2	485	495	4	2827	2833	-12	582	552	-7	944	952
1	885	818	5	2009	2004	-10	1201	1276	-5	598	603
3	1075	1031	6	2494	2447	-8	1029	1020	-3	433	468
5	1069	1059	7	1659	1692	-7	567	642	-2	664	691
6	830	782	8	1073	1143	-6	1904	1938	0	1674	1695
8	817	851	10	1296	1260	-5	647	623	1	614	629
9	349	399	12	561	610	-4	331	371	2	1587	1589
10	591	580	* H= 2 K= -1			-3	760	751	3	755	717
* H= 2 K= -4			-8	760	715	-2	787	813	4	611	589
-9	657	677	-6	869	873	-1	1467	1516	5	1192	1255
-7	1502	1546	-4	2949	2956	0	1849	1934	7	1279	1267
-6	551	553	-3	2061	1932	1	1523	1431	9	616	639
-5	408	396	-2	1481	1410	2	1956	1987	12	704	732
-4	1565	1541	-1	4949	5072	3	412	411	* H= 2 K= 6		
-3	358	319	0	634	721	4	1051	994	-3	464	534
-2	1607	1506	1	1435	1444	5	667	746	-2	855	817
0	1079	1011	2	1407	1322	6	537	482	0	823	880
1	929	924	3	2107	2205	7	1161	1127	2	555	553
3	1012	1056	4	967	1059	9	491	472	3	375	382
5	787	831	5	1790	1809	* H= 2 K= 3			5	542	476
7	476	489	6	977	1037	-12	764	724	7	372	372
8	756	758	8	1306	1320	-10	1211	1192	8	369	409
9	460	219	10	1134	1156	-9	692	495	10	405	402
11	702	529	11	1013	1046	-8	1606	1656	12	457	362
13	709	721	13	630	602	-6	490	471	* H= 2 K= 7		
* H= 2 K= -3			* H= 2 K= 0			-5	930	937	-11	417	407
-14	763	410	-11	579	432	-4	1849	1867	-9	475	507
-11	735	757	-9	681	657	-3	1938	1893	-7	719	794
-10	736	466	-7	807	818	-2	1569	1601	-6	414	384
-9	1499	1483	-4	625	648	-1	3115	2997	-5	444	456
-7	1630	1669	-3	1805	1861	0	2506	2496	-4	635	703
-6	1932	1994	-2	938	900	1	867	915	-3	393	447
-5	1351	1311	-1	2569	2615	2	2020	2553	-2	457	454
-4	1836	1947	0	1796	1752	3	633	641	-1	515	525
-2	2394	2431	1	1475	1430	4	1644	1573	1	534	537
0	948	1057	2	643	641	5	632	639	2	393	374
1	423	279	3	1744	1678	6	736	751	3	559	538
2	1063	918	4	2305	2172	7	414	423	5	643	669
3	2539	2543	5	761	696	10	495	561	6	360	376
4	734	719	6	2157	2252	11	626	673	* H= 2 K= 8		
5	512	533	7	925	857	* H= 2 K= 4			-11	473	457
6	941	891	8	1042	1057	-12	537	493	-9	614	623
8	1007	931	9	756	788	-10	630	727	-8	754	691
10	875	917	11	855	862	-8	630	665	-7	467	529
11	647	633	13	776	733	-7	607	633	-6	852	905
* H= 2 K= -2			* H= 2 K= 1			-5	1796	1796	-4	876	923

-1	569	523	* H= 3 K= -8			4	410	490	-5	1478	1379	
1	1033	1004	-11	344	214	5	614	642	-4	2324	2339	
2	582	569	-8	350	362	6	287	225	-3	827	874	
3	1178	1223	-6	446	479	7	787	834	-2	1814	1722	
5	327	410	-5	453	421	8	467	384	-1	1499	1376	
* H= 2 K= 9			-4	677	680	9	643	661	0	1287	1245	
-8	617	612	-3	984	1037	10	847	825	1	1161	957	
-6	751	775	-2	653	661	12	536	551	2	571	565	
-4	1031	1057	-1	765	847	* H= 3 K= -4			3	2596	2690	
-3	539	593	1	926	993	-12	638	675	4	1088	1142	
-2	883	874	2	600	562	-10	1143	1128	5	2665	2596	
-1	633	623	3	1150	1226	-9	490	494	6	345	295	
0	396	393	4	1439	1475	-8	799	885	7	1805	1864	
1	550	548	5	1001	1011	-7	1471	1506	8	564	657	
3	594	643	6	722	702	-6	368	437	9	1050	1084	
4	722	741	7	332	307	-5	1895	1851	10	764	792	
6	589	579	9	612	633	-4	450	552	12	1001	960	
* H= 2 K= 10			11	580	565	-3	1319	1350	* H= 3 K= -1			
-6	545	478	13	434	390	-2	839	797	-10	574	522	
-3	553	570	* H= 3 K= -7			-1	692	600	-7	339	747	
-1	607	594	-7	565	584	0	1230	1174	-6	367	338	
1	420	452	-5	588	580	1	248	180	-4	807	805	
2	556	540	-3	386	449	2	2370	2358	-3	635	550	
3	466	432	-1	677	703	3	941	921	-2	997	901	
4	628	610	0	755	749	4	987	1013	-1	416	476	
5	393	345	1	683	640	5	843	910	0	613	580	
6	752	720	2	835	843	6	658	722	1	1055	812	
* H= 2 K= 11			3	849	862	7	605	600	2	1273	1207	
4	456	447	4	1233	1260	9	511	528	3	991	947	
* H= 3 K=-12			6	655	708	10	923	913	4	425	446	
4	335	274	7	675	629	15	389	389	5	1566	1519	
* H= 3 K=-11			9	569	710	* H= 3 K= -3			6	1302	1339	
-4	417	392	11	612	649	-12	454	409	7	532	589	
-2	340	418	* H= 3 K= -6			-10	559	570	8	1127	1119	
1	361	445	-10	582	520	-9	1051	1011	10	1203	1173	
3	520	562	-8	318	351	-7	1162	1084	12	484	503	
4	480	446	-1	620	585	-6	493	436	13	362	332	
* H= 3 K=-10			1	264	164	-5	2213	2125	* H= 3 K= 0			
-9	423	427	2	1041	991	-4	1312	1315	-9	407	426	
-7	418	399	3	1274	1256	-3	2056	2043	-7	334	816	
-6	410	469	4	346	349	-2	572	456	-6	772	718	
-4	607	587	5	1178	1223	-1	637	481	-4	224	245	
-1	549	479	6	816	650	0	2502	2502	-3	315	787	
1	1042	996	7	1092	1079	1	334	183	-2	1049	909	
3	564	570	8	394	377	2	2542	2433	-1	1086	1793	
6	536	557	10	395	396	3	1675	1582	1	1474	1287	
8	526	55	12	468	465	4	836	746	2	731	852	
* H= 3 K= -9			13	394	329	5	2141	2081	3	767	736	
-7	496	507	* H= 3 K= -5			7	1393	1417	4	720	724	
-6	627	702	-10	464	459	8	484	513	6	111	1104	
-4	511	539	-8	643	637	9	1241	1305	8	793	766	
-3	530	502	-7	778	824	10	560	556	10	438	425	
-2	794	793	-5	805	766	12	637	555	13	516	504	
-1	1152	1165	-3	954	921	14	410	387	* H= 3 K= 1			
0	554	557	-2	1029	936	* H= 3 K= -2			-11	604	635	
1	1110	1041	-1	922	919	-11	370	413	-10	660	695	
3	887	909	0	1539	1516	-9	581	555	-9	1122	1162	
4	487	446	1	539	519	-8	474	456	-8	649	678	
6	681	716	2	991	485	-7	501	606	-7	816	841	
8	482	535	3	884	863	-6	590	599	-6	559	610	

-4	1866	1950	-1	1195	1241	7	505	495	-5	458	445	
-3	1279	1329	0	573	626	10	357	301	-4	345	324	
-2	1343	1303	1	1070	1046	* H= 3 K= 9			-3	629	558	
-1	1264	1310	2	1643	1569	-7	367	438	-2	315	320	
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2	809	874	5	486	577	-3	322	226	1	491	531	
3	1477	1524	6	1759	1770	-2	624	698	2	811	875	
4	348	354	7	477	427	0	428	458	3	381	422	
6	426	474	9	808	830	1	668	640	4	388	420	
8	808	750	11	756	727	3	755	722	6	766	810	
9	485	482	13	617	602	5	906	922	7	569	581	
* H= 3 K= 2			* H= 3 K= 5			7	437	500	9	646	622	
-13	739	730	-10	419	429	8	579	559	11	474	547	
-11	748	769	-5	709	689	* H= 3 K= 10			* H= 4 K= -6			
-10	455	450	-3	768	791	0	394	477	-11	587	619	
-9	557	551	-2	719	753	5	426	434	-6	610	630	
-8	770	748	-1	1141	1083	6	395	388	-5	518	475	
-7	305	325	0	374	369	* H= 4 K=-12			-4	699	622	
-6	1295	1274	2	1117	1176	-2	446	443	-3	478	557	
-5	1394	1441	3	409	373	0	483	521	-1	809	797	
-4	2958	2956	4	889	932	5	436	406	0	950	1014	
-3	1705	1591	9	465	461	* H= 4 K=-11			1	926	924	
-2	1446	1376	11	497	506	-2	533	470	2	1088	1114	
-1	2892	2946	* H= 3 K= 6			0	559	565	3	306	347	
0	271	183	-12	476	495	3	467	534	4	614	581	
1	2589	2481	-10	476	458	5	431	420	6	485	497	
2	951	1039	-7	491	508	* H= 4 K=-10			7	1068	1104	
3	2034	1990	-6	723	779	-5	520	445	8	555	570	
4	277	330	-5	518	902	-4	524	535	9	1041	1076	
5	1540	1521	-4	339	278	-3	614	604	11	414	409	
7	1298	1262	0	971	983	-2	729	731	* H= 4 K= -5			
8	527	513	1	527	486	0	737	730	-10	533	529	
9	1052	1108	2	593	551	2	510	599	-8	1581	1613	
10	453	553	4	323	327	3	748	741	-6	1543	1550	
11	775	753	7	443	469	5	604	598	-5	453	477	
* H= 3 K= 3			9	504	453	* H= 4 K= -9			-4	1005	1024	
-8	1041	1039	* H= 3 K= 7			-6	580	550	-3	650	657	
-7	508	525	-10	532	536	-5	521	517	-2	385	376	
-6	1655	1687	-9	422	478	-4	707	784	-1	1245	1263	
-4	1635	1609	-7	935	1011	-2	715	789	0	1331	1320	
-3	1821	1738	-5	711	743	0	830	835	1	1566	1583	
-2	644	454	-4	533	345	1	621	620	3	1310	1329	
-1	2166	2201	-2	738	703	2	732	743	4	1109	1147	
0	825	801	0	833	896	3	850	740	5	542	566	
1	1545	1516	2	692	706	5	559	532	6	1106	1159	
2	1208	1117	3	640	657	8	746	730	7	562	580	
3	947	939	4	691	688	10	648	605	8	521	534	
4	1239	1227	5	1025	1021	* H= 4 K= -8			9	1[illegible]	[illegible]	
6	1434	1467	* H= 5 K= 8			-4	437	485	12	534	560	
7	558	554	-9	592	545	-3	670	653	[illegible]			
8	1014	994	-7	580	665	-2	564	540	-11	135	131	
9	906	1046	-5	809	830	-1	757	780	-10	1394	1396	
10	443	464	-4	729	747	0	564	605	-9	357	339	
11	837	763	-3	593	756	1	710	760	-8	1245	1183	
13	475	521	-2	857	858	3	942	921	-6	986	1001	
* H= 3 K= 4			0	653	657	5	613	588	-5	344	834	
-10	420	423	1	815	815	6	941	969	-4	1330	1304	
-8	586	599	2	910	895	12	402	386	-3	910	962	
-4	435	361	3	1084	1117	* H= 4 K= -7			-2	413	490	
-3	1357	1352	5	909	914	-9	436	405	-1	1560	1422	

0	288	266	-1	696	698	-1	1410	1395	1	676	674
1	957	859	0	1074	965	0	1088	1079	2	1050	1129
2	3143	2994	1	315	299	1	1649	1591	3	365	402
3	464	420	2	863	716	2	1527	1507	4	823	777
4	2400	2354	3	816	968	3	1125	1236	6	398	410
5	394	357	5	847	860	4	393	437	7	459	465
6	1086	1091	6	627	714	5	1504	1604	* H= 4 K= 7		
7	516	587	7	540	546	6	1101	1284	-10	486	500
8	480	526	8	427	458	7	1117	1180	-7	617	590
9	874	911	10	932	904	8	765	769	-6	405	425
10	335	342	12	674	703	10	1000	1065	-5	736	786
11	795	746	* H= 4 K= 0			13	427	422	-3	826	806
13	512	560	-14	582	526	* H= 4 K= 3			-1	779	851
* H= 4 K= -3			-12	580	657	-11	562	469	0	1393	1390
-7	733	745	-10	587	630	-9	454	474	1	907	868
-6	422	470	-9	628	662	-8	595	518	2	1604	1648
-5	319	285	-7	934	957	-6	720	770	4	904	898
-3	1436	1531	-6	917	931	-5	576	592	* H= 4 K= 8		
-2	804	721	-5	1671	1374	-4	1018	1643	-5	516	522
-1	769	799	-4	1638	1668	-2	1182	1215	-3	661	637
0	1634	1602	-3	940	899	-1	738	896	-2	569	575
1	350	364	-2	931	874	1	955	970	-1	695	730
2	3499	3348	0	1548	1542	3	1544	1539	0	689	762
4	2269	2264	2	511	464	5	713	760	2	737	739
5	349	446	3	913	1022	6	993	1052	3	347	343
6	1617	1641	4	293	166	8	1386	1376	4	642	634
7	1207	1238	5	779	711	10	850	823	5	641	565
8	959	1048	6	617	589	12	536	574	6	429	434
9	1317	1371	8	1004	1005	13	468	445	7	707	698
11	803	784	10	680	661	* H= 4 K= 4			9	507	519
14	424	398	15	374	346	-8	528	550	* H= 4 K= 9		
* H= 4 K= -2			* H= 4 K= 1			-5	704	749	2	514	496
-7	666	675	-12	641	630	-4	463	448	4	563	491
-5	1059	1047	-11	519	526	-1	1349	1297	5	414	452
-4	867	822	-9	524	510	1	936	895	* H= 5 K=-12		
-3	726	631	-6	792	766	3	542	451	-1	361	404
-2	556	583	-7	1382	1369	4	511	532	* H= 5 K=-11		
-1	521	440	-6	1037	1117	5	522	534	-8	463	421
0	389	513	-5	2044	2129	6	643	657	-1	515	562
1	590	625	-4	1026	1563	8	1159	1184	0	397	427
2	1262	1268	-3	527	516	10	397	393	2	486	575
3	922	1001	-2	1565	1519	* H= 4 K= 5			7	421	358
4	826	854	-1	278	281	-8	547	573	* H= 5 K=-10		
5	416	439	0	1497	1496	-7	423	409	-5	427	403
6	1053	1059	1	1946	1926	-6	617	613	-3	537	526
7	1022	908	3	1317	1354	-3	666	741	-2	554	541
[illegible]			[illegible]			-1	1035	1024	-1	774	744
9	856	844	6	1013	1195	1	542	554	0	642	616
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12	567	543	8	527	535	7	289	309	2	534	527
14	499	529	9	539	542	11	407	389	4	336	368
* H= 4 K= -1			13	586	575	* H= 4 K= 6			7	674	650
-10	568	518	* H= 4 K= 2			-10	507	579	9	609	648
-9	426	473	-11	587	605	-8	775	770	* H= 5 K= -9		
-8	763	763	-9	566	595	-6	620	647	-4	699	675
-7	569	599	-7	771	781	-5	713	711	-3	431	407
-6	246	221	-6	570	752	-4	416	432	-2	614	657
-5	499	507	-4	2119	2127	-3	823	835	0	569	574
-3	463	332	-3	457	559	-1	462	457	2	543	554
-2	654	656	-2	2918	3005	0	566	547	3	461	460

5	702	742	1	2400	2503	-3	1417	1426	-2	953	980
7	525	593	2	498	552	-1	702	725	0	751	842
9	577	593	3	2011	2496	0	652	719	1	331	154
* H= 5 K= -8			5	946	956	1	337	450	2	794	799
-1	677	693	6	874	874	2	1520	1429	3	733	844
1	784	790	8	758	664	4	725	706	4	287	406
2	675	742	10	410	366	5	974	978	5	1265	1241
3	1025	1044	* H= 5 K= -4			7	790	841	6	385	846
6	528	547	-8	503	481	9	633	704	7	1677	1685
8	908	982	-6	524	546	10	439	513	8	640	632
9	340	290	-4	970	1016	12	706	670	9	1220	1227
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12	368	367	-1	1684	1707	-12	562	489	12	550	565
* H= 5 K= -7			1	2533	2725	-10	730	808	* H= 5 K= 3		
-9	396	462	3	916	848	-9	327	366	-5	482	493
-7	852	848	4	808	804	-8	964	923	-4	328	369
-5	374	397	5	976	962	-7	965	925	-2	911	975
-3	569	552	6	1387	1394	-6	806	834	0	778	770
-2	737	767	8	1241	1227	-5	1630	1658	1	1150	1056
-1	1051	1040	10	662	658	-4	504	446	3	701	736
0	846	837	13	704	699	-3	1654	1844	5	1023	1006
1	870	892	15	586	585	-2	565	594	8	591	590
3	410	453	* H= 5 K= -3			-1	1118	1166	9	422	439
4	819	830	-5	437	412	0	944	982	10	619	543
5	614	628	-4	378	434	1	685	673	12	422	389
6	953	969	-3	464	398	2	2020	2040	* H= 5 K= 4		
8	646	691	-1	1512	1401	3	814	845	-7	519	563
10	471	456	0	293	335	4	852	870	-5	764	762
11	305	285	2	520	596	5	1627	1657	-4	789	822
12	365	350	4	1389	1450	6	1226	1246	-2	721	748
13	503	535	5	353	363	7	1080	1131	1	750	712
* H= 5 K= -6			6	1417	1489	9	516	449	3	369	374
-11	470	436	8	696	713	10	382	344	10	325	365
-9	538	559	9	600	596	12	542	555	11	337	321
-7	612	644	11	742	673	14	330	328	* H= 5 K= 5		
-6	880	977	* H= 5 K= -2			* H= 5 K= 1			-11	376	445
-5	489	543	-11	330	322	-10	474	443	-9	487	465
-4	1423	1454	-8	438	487	-8	324	377	-7	627	649
-3	310	290	-7	660	670	-7	725	791	-6	993	1012
-2	1322	1369	-5	795	785	-6	346	366	-4	770	753
-1	261	232	-4	395	332	-5	2461	2573	-2	571	560
0	857	821	-2	434	525	-4	597	636	-1	1199	1204
1	524	533	-1	371	365	-3	1622	1701	0	569	497
3	1707	1637	0	1466	1459	-2	1243	1257	1	1102	1082
5	1240	1249	1	539	542	-1	946	960	6	789	824
6	471	490	2	1195	1196	0	1802	1782	9	304	299
9	[illegible]	[illegible]	[illegible]			1	1223	1245	* H= 5 K= 6		
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11	559	611	[illegible]			3	431	427	-6	554	573
* H= 5 K= -5			[illegible]			4	1303	1280	-4	922	904
-11	558	567	9	1383	1351	5	902	871	-3	986	1037
-9	632	674	11	509	514	7	1557	1536	-2	226	91
-8	512	487	* H= 5 K= -1			9	1121	1108	-1	1525	1554
-7	671	659	-13	480	469	10	406	366	0	711	764
-6	1052	1036	-12	356	367	11	602	547	1	969	1042
-5	603	524	-10	605	603	* H= 5 K= 2			3	931	947
-4	1048	1111	-9	1382	1374	-9	421	441	4	969	985
-2	807	799	-7	841	841	-8	448	452	5	417	366
-1	847	873	-6	951	951	-7	721	722	6	561	587
0	522	517	-5	747	814	-5	673	675	8	573	517

* H=	5 K=	7	7	443	556	-9	863	915	3	517	527	
-6	595	568	9	406	428	-8	646	755	4	1067	1116	
-4	650	703	10	542	543	-7	798	809	6	1513	1519	
-3	555	512	12	543	465	-6	697	757	7	648	632	
-2	486	523	* H=	6 K=	-6	-4	455	507	8	516	522	
-1	858	873	-7	788	738	-3	724	678	9	699	727	
1	806	810	-5	991	1012	-2	732	799	11	554	544	
2	636	599	-4	607	644	-1	792	821	* H=	6 K=	2	
3	621	638	-3	891	946	1	806	665	-3	343	361	
4	629	665	-2	1100	1075	2	1028	1050	0	630	634	
5	472	354	-1	392	421	3	820	834	2	877	850	
6	718	698	0	1849	1769	4	1485	1591	3	325	288	
8	539	510	1	964	946	5	550	577	4	752	803	
* H=	5 K=	8	2	1530	1534	6	574	576	5	710	681	
1	699	723	5	1109	1062	9	823	844	9	777	725	
3	306	283	7	814	807	11	807	825	10	345	375	
4	422	433	9	545	596	* H=	6 K=	-1	* H=	6 K=	3	
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* H=	6 K=	-12	* H=	6 K=	-5	-10	510	486	-5	1317	1396	
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* H=	6 K=	-11	-4	569	676	-8	889	837	0	526	579	
-1	501	443	-2	1847	1856	-6	1327	1284	2	604	596	
6	650	637	0	1057	1053	-4	1452	1366	3	467	481	
8	451	424	3	1398	1369	-3	759	707	7	491	575	
* H=	6 K=	-10	5	1589	1659	-2	652	651	10	364	369	
-5	393	358	7	777	763	-1	1697	1656	* H=	6 K=	4	
0	553	560	8	380	358	0	676	642	-9	590	575	
2	384	374	10	567	640	1	1646	1634	-8	624	566	
6	490	503	12	850	856	2	1037	990	-7	644	654	
8	378	482	14	465	525	3	691	634	-5	1028	1020	
* H=	6 K=	-9	* H=	6 K=	-4	4	1271	1321	-4	943	980	
-7	529	466	-6	463	436	5	534	560	-3	647	711	
-4	376	376	-4	632	599	6	917	916	-2	1019	1004	
-2	636	571	-3	410	449	7	339	358	-1	535	497	
-1	534	555	-1	944	915	8	623	637	0	575	490	
0	701	680	0	267	264	9	862	870	3	674	696	
2	577	618	1	2042	2075	10	311	352	5	923	877	
7	681	689	2	671	686	11	572	593	10	442	458	
* H=	6 K=	-8	3	1525	1461	* H=	6 K=	0	* H=	6 K=	5	
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-3	478	447	5	292	419	-6	1051	1069	-7	594	659	
0	540	543	6	776	763	-4	1093	1126	-6	454	434	
1	517	598	8	1054	1064	-3	1054	1060	-5	466	539	
2	803	911	10	567	656	-1	1912	1904	-4	947	959	
3	1009	1083	* H=	6 K=	-3	0	677	655	-3	771	751	
5	547	531	-8	464	410	1	944	992	-2	1261	1324	
7	767	788	-7	594	599	2	835	1044	0	1121	1186	
9	426	394	-6	551	518	3	937	932	2	781	751	
10	653	603	-5	284	273	4	1747	1787	3	867	894	
* H=	6 K=	-7	-4	838	838	5	2055	2101	5	933	923	
-6	451	471	-1	539	548	6	1506	1511	7	594	625	
-7	495	505	0	342	384	* H=	6 K=	1	8	491	474	
-5	916	952	1	820	860	-5	669	702	9	429	427	
-3	647	621	4	777	761	-4	594	653	* H=	6 K=	6	
-2	457	537	6	1505	1571	-5	451	395	-7	445	416	
0	1231	1258	8	906	954	-3	833	836	-5	336	389	
2	1169	1141	11	471	513	-1	831	824	-4	540	521	
3	328	291	13	921	927	0	1126	1176	-2	1214	1177	
4	551	661	* H=	6 K=	-2	1	395	394	-1	532	527	
5	619	653	-11	497	522	2	996	1021	0	1135	1140	

1	711	757	3	397	468	5	1828	1935	4	843	923	
2	653	627	5	943	892	6	544	576	5	640	644	
5	697	680	7	859	937	7	1130	1151	6	499	598	
7	662	642	9	547	540	11	402	380	7	599	693	
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* H= 6 K= 7			* H= 7 K= -4			-6	1063	1013	* H= 7 K= 5			
1	403	443	-4	702	726	-5	485	492	-5	627	621	
3	392	427	-2	670	657	-4	790	853	-3	646	639	
* H= 7 K=-11			0	613	601	-2	923	935	-2	677	713	
5	428	502	1	469	513	-1	330	326	-1	1065	1050	
* H= 7 K=-10			3	1365	1414	1	932	859	0	719	829	
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1	532	492	8	615	669	4	349	389	2	616	607	
6	515	544	10	658	650	5	1122	1155	4	615	616	
* H= 7 K= -9			12	619	592	6	543	519	5	483	491	
2	668	680	* H= 7 K= -3			8	726	745	6	574	524	
4	504	503	-10	374	398	9	418	400	7	722	737	
7	421	441	-9	514	462	10	561	607	9	647	579	
9	672	620	-6	314	305	11	392	419	* H= 7 K= 6			
* H= 7 K= -8			-5	1135	1201	* H= 7 K= 1			2	513	526	
-7	365	351	-4	758	756	-6	550	670	3	536	509	
-6	683	693	-3	729	685	-1	474	542	4	408	399	
-3	664	697	-2	435	463	1	666	663	5	467	437	
-1	768	773	-1	406	387	2	915	921	7	411	471	
1	668	683	1	1016	1105	3	340	382	* H= 7 K= 8			
2	486	415	2	581	679	4	718	782	-2	484	509	
4	652	647	3	1365	1397	6	728	730	* H= 8 K=-12			
6	525	526	5	784	815	8	808	810	5	426	400	
7	399	425	6	669	660	9	323	339	* H= 8 K=-11			
8	434	419	8	883	898	11	483	479	-4	341	324	
9	477	525	10	692	690	* H= 7 K= 2			3	624	604	
11	335	358	13	366	340	-5	517	601	5	525	541	
* H= 7 K= -7			* H= 7 K= -2			-4	552	564	* H= 8 K=-10			
-5	656	681	-11	540	512	-3	1118	1156	-2	470	445	
-3	1431	1398	-9	827	840	-1	585	626	0	336	337	
-1	1549	1542	-7	807	861	2	581	572	4	462	521	
1	675	602	-5	1239	1196	4	899	893	6	587	530	
2	307	332	-4	559	566	6	342	351	8	534	514	
4	1114	1114	-2	1169	1199	11	451	470	* H= 9 K= -9			
6	685	655	-1	993	910	* H= 7 K= 3			-4	636	601	
9	550	486	0	1595	1576	-6	764	771	-2	622	558	
* H= 7 K= -6			1	943	980	-5	736	755	3	466	466	
-7	502	575	2	1157	1181	-5	779	794	5	442	450	
-5	347	362	3	1006	1002	-4	542	612	8	535	509	
-3	544	518	5	1142	1170	-3	1217	1237	* H= 9 K= -8			
-2	372	364	6	658	653	-2	367	335	-6	420	441	
-1	704	732	7	655	600	2	677	624	-5	314	309	
0	[illegible]		[illegible]			[illegible]			[illegible]			
1	552	[illegible]	10	543	577	6	526	575	-2	571	[illegible]	
2	[illegible]		[illegible]			[illegible]			[illegible]			
4	[illegible]		[illegible]			[illegible]			1	744	782	
7	597	637	-6	868	827	-6	694	631	5	661	707	
9	734	635	-4	1573	1461	-7	515	546	5	611	569	
11	757	789	-3	356	393	-5	610	640	6	521	524	
* H= 7 K= -5			-2	1529	1474	-3	1261	1296	8	561	563	
-7	470	531	-1	884	869	-2	437	439	10	482	463	
-2	1003	1039	0	1007	1026	-1	1171	1161	* H= 9 K= -7			
0	1027	1053	1	1573	1574	0	661	579	-4	437	461	
1	397	510	2	426	441	1	670	573	-2	560	562	
2	711	696	3	1441	1419	2	710	695	-1	741	784	

1	686	681	* H= 8 K= -2		-9	654	619	-2	374	292
4	490	426	-10	415	403	-8	597	571	-1	684	635
5	430	418	-7	356	352	-7	353	418	1	490	510
6	673	673	-5	673	702	-6	992	894	2	525	578
8	630	623	-3	1359	1403	-4	470	530	4	753	714
10	468	487	-2	454	528	-2	776	748	6	697	681
* H= 8 K= -6			-1	332	401	-1	855	823	8	543	556
-5	605	579	0	1215	1191	0	506	505	9	336	311
-3	552	611	1	377	418	1	743	818	* H= 9 K= -5		
-1	448	476	2	1576	1600	2	440	454	-4	444	486
2	847	866	3	559	553	3	716	675	-3	684	693
3	368	269	4	1465	1407	4	841	790	-1	852	931
4	913	885	6	349	403	5	477	442	2	445	439
6	640	656	7	541	547	6	921	893	4	643	653
8	606	575	8	594	634	8	678	663	6	595	610
9	480	534	9	747	766	* H= 8 K= 4			7	368	379
11	593	586	10	483	490	-6	594	568	9	482	544
* H= 8 K= -5			11	505	536	-5	360	380	11	684	606
-6	403	395	* H= 8 K= -1			-2	382	388	* H= 9 K= -4		
-5	717	699	-7	541	531	-1	685	677	-9	379	340
-3	404	383	-5	539	545	1	891	835	-6	723	733
0	995	1007	-4	311	356	2	768	732	-5	337	367
2	1434	1437	-3	586	560	3	733	768	-4	984	1030
4	747	780	-2	899	893	4	867	830	-2	670	734
5	429	435	0	1287	1295	5	507	469	-1	792	811
7	424	441	2	1029	1025	6	646	578	1	1060	1049
9	599	565	3	590	553	8	653	673	3	490	477
11	486	452	4	533	486	9	353	387	6	525	506
* H= 8 K= -4			5	673	675	* H= 8 K= 5			7	588	599
-8	473	499	7	1081	1082	1	519	529	8	467	497
-6	577	540	8	393	468	4	427	463	9	519	541
-5	509	539	9	418	450	6	434	398	* H= 9 K= -3		
-3	575	621	* H= 8 K= 0			8	448	414	-8	341	425
-2	619	649	-4	420	424	* H= 8 K= 6			-6	723	717
-1	757	827	-2	522	564	2	357	280	-3	520	552
0	726	708	3	917	912	* H= 9 K=-11			-1	1250	1194
1	506	481	4	522	466	2	348	387	1	1413	1389
2	484	517	5	1199	1231	5	417	435	2	483	489
5	1300	1283	6	432	403	* H= 9 K=-10			3	536	572
7	770	777	10	608	606	7	480	493	4	381	387
9	461	447	12	504	466	* H= 9 K= -9			6	665	602
12	487	516	* H= 8 K= 1			2	490	469	7	417	417
* H= 8 K= -3			-4	782	771	4	576	617	8	697	692
-10	703	720	-1	913	560	5	638	611	9	595	587
-8	833	805	1	864	835	7	373	430	11	453	451
-5	468	505	3	707	613	* H= 9 K= -8			* H= 9 K= -2		
-3	1389	1362	6	599	645	-4	415	385	-5	478	454
-2	615	583	8	556	562	-2	423	456	-4	449	446
-1	1276	1302	10	562	617	0	432	423	-3	391	387
0	576	557	* H= 8 K= 2			3	598	604	-1	756	758
1	496	510	-9	590	586	5	675	615	0	379	391
2	933	960	-6	578	536	7	492	472	1	490	471
3	679	651	-4	796	843	* H= 9 K= -7			2	923	911
4	988	1011	-2	714	701	-4	511	480	4	1207	1132
5	742	734	-1	607	579	-2	331	398	6	612	589
6	424	411	1	352	743	1	563	574	9	563	535
7	398	405	3	462	546	3	699	713	11	663	658
9	344	282	6	809	791	8	623	567	* H= 9 K= -1		
10	504	526	8	511	500	* H= 9 K= -6			-5	655	589
12	525	507	* H= 8 K= 3			-3	692	637	2	484	463

4	548	529	*	H= 10	K=-10		-3	661	632		5	581	628					
5	604	622		-1	362	369		-1	536	531		7	749	746					
9	519	523		2	344	306		2	643	683		9	560	487					
11	513	443		4	466	461		3	545	459	*	H= 11	K= -3					
* H= 9	K= 0		*	H= 10	K= -9			4	860	848		-4	576	539					
-7	369	419		2	642	622		5	443	473		3	489	476					
-2	501	522		4	449	520		6	524	539		5	513	492					
-1	557	563	*	H= 10	K= -8		*	H= 10	K= 0		*	H= 11	K= -2					
0	888	914		5	559	554		-5	478	468		-4	401	362					
1	510	511		7	537	459		-3	596	640		-1	383	365					
2	646	618	*	H= 10	K= -7			0	603	605		1	676	677					
3	429	406		-4	499	497		1	348	343		6	557	586					
5	780	768		-2	577	595		2	964	911	*	H= 11	K= -1					
7	659	686		1	389	329		4	679	617		-1	645	671					
12	431	327		3	585	541		7	411	439		1	705	656					
* H= 9	K= 1			5	675	604	*	H= 10	K= 1			4	470	435					
-9	568	520		7	529	442		-6	552	527		6	478	506					
-7	536	550	*	H= 10	K= -6			-3	506	489		8	424	454					
-5	518	533		-5	472	392		-1	652	599	*	H= 11	K= 0					
-4	505	452		-1	360	377		0	651	676		-4	536	469					
-3	401	377		0	480	475		1	928	901		-2	467	537					
-2	1016	958		1	462	521		2	849	751		-1	748	693					
0	837	652		5	555	550		4	543	486		0	577	502					
2	449	410		8	661	619	*	H= 10	K= 2			1	603	594					
3	556	496		10	472	450		-3	470	493		4	519	433					
5	595	552	*	H= 10	K= -5			-2	483	392	*	H= 11	K= 1					
7	674	611		-7	548	558		-1	571	512		-1	453	473					
8	516	463		-5	506	467		0	536	546		1	667	654					
* H= 9	K= 2			-2	759	721		2	702	648		3	654	620					
-7	614	632		0	749	786		4	588	616	*	H= 11	K= 2						
-5	320	734		1	436	469		5	622	591		0	425	362					
-3	621	576		2	548	499		6	436	434	*	H= 12	K= -8						
-2	446	413		8	567	535		7	503	473		2	355	313					
0	605	596	*	H= 10	K= -4		*	H= 10	K= 3			4	459	493					
1	840	776		-4	585	627		1	366	320	*	H= 12	K= -7						
2	762	749		-2	901	863		2	384	412		0	338	299					
3	1138	1052		0	426	490		3	351	389	*	H= 12	K= -6						
4	609	632		1	596	650		7	435	390		1	443	421					
5	710	655		3	680	629	*	H= 11	K= -8			0	430	455					
7	359	368		6	338	375		2	543	519	*	H= 12	K= -5						
8	563	562		7	474	424	*	H= 11	K= -7			-3	387	410					
* H= 9	K= 3			8	656	628		2	386	360		4	370	426					
-4	541	572	*	H= 10	K= -3			5	488	551	*	H= 12	K= -4						
-2	363	376		-4	794	731		7	511	587		-2	381	348					
0	589	605		1	717	701	*	H= 11	K= -6			0	495	456					
1	883	850		3	753	750		2	574	509		5	479	466					
2	565	566		5	494	424		4	470	536		7	560	518					
3	858	816		8	703	731	*	H= 11	K= -5		*	H= 12	K= -2						
5	805	778		10	576	536		-3	650	638		-2	37	590					
7	576	562	*	H= 10	K= -2			4	485	485		0	436	396					
* H= 9	K= 4			-1	798	780		5	459	440	*	H= 12	K= -1						
5	415	470		1	606	643		7	558	493		0	443	395					
6	353	358		4	410	391		9	383	410	*	H= 12	K= 0						
* H= 9	K= 5			6	461	486	*	H= 11	K= -4			0	517	542					
2	389	293	*	H= 10	K= -1			-2	511	541		2	382	350					

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